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Number Two

THE WORLD WIDE CHEMICAL TRANSLATION SERIES

Edited by E. EMMET REID

Professor of Organic Chemistry, The Johns Hopkins University

ORGANIC LABORATORY METHODS

BY

The Late PROFESSOR LASSAR-COHN (Königsberg)

AUTHORIZED TRANSLATION
FROM THE GENERAL PART OF
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TRANSLATOR'S PREFACE

Lassar-Cohn's *Arbeitsmethoden für Organisch-Chemische Laboratorien* appeared in the original German in two volumes. The first deals with the general operations of laboratory technique such as distillation, crystallization, etc., the second with general organic reactions, such as nitration, sulfonation and so on. The author's preface concerned itself almost entirely with the second volume, and since the present translation will be limited to the first volume, there seems little point in reproducing a preface not very apropos.

There has been a noticeable lack of works in English dealing with the material so well covered by the German compilations of the organic field, and in the absence of an original work in our language the translator trusts that the present volume may find a welcome in many quarters.

The work makes no claims as to completeness. The field is too large and new methods are appearing almost every day. Nor does it pose as a text book for beginners. Its aim, rather is to cite and outline the methods by which typical difficulties have been overcome and leave the adaptation of the suggestions to the problem at hand to the resourcefulness of the reader.

Dr. Lassar-Cohn died in October, 1922, and did not see the proof of the fifth edition of his work. Consequently, the translator has been deprived of the helpful criticism which the author would surely have given, and he trusts that any errors in the interpretation of the author's ideas may be ascribed to these circumstances.

This translation has only been made possible because of the unfailing encouragement and material assistance of the translator's wife and he acknowledges her services with gratitude.

Ralph E. Oesper

Cincinnati, July, 1928

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CHAPTER I

STARTING MATERIALS AND EXTRACTION

STARTING MATERIALS

The various starting materials for organic chemical work should be of the highest purity obtainable and, when possible, the quantities in the ratio of their molecular weights. In those cases in which the use of an excess of one or more of the starting materials is deemed necessary it is customary to take the excess in the form of a multiple of the molecular weight. It is easy then in the repetition of an experiment to determine what excess gives the best results.

Liquid reagents whose specific gravities are known are not weighed, especially if they attack the mucous membranes, but are measured in calibrated vessels. This procedure considerably simplifies working with bromine, for example. 1 cc. of this is taken as equal to 3 grams. Furthermore, in dealing with small quantities of benzoyl chloride, etc., these are best delivered from the stock bottle through a narrow tube calibrated clear to the tip, and the quantity thus determined allowed to flow into the material to be worked up.

If the specific gravity of liquids is not known the following method may be used which is preferable to direct weighing of small quantities of liquids, particularly those that are easily volatile, like methyl iodide, etc. This consists in weighing the liquid in a dropping bottle of the form illustrated (fig. 1), which also serves as a storage vessel; 10 or 20 drops are removed, and the weighing repeated. The weight of a single drop is then known, and even fractions of a gram of the liquid may thus be conveniently added to the reaction mixture.

If it is necessary to place accurately weighed, small quantities of volatile liquids such as bromine in tubes which are to be sealed, approximately the required quantity is weighed in a sealed bulb. Then the quantity of other material to be sealed with it is calculated from this weight already determined. Thus are avoided all the inconveniences accompanying the exact weighing of a definite small quantity of volatile material and also the loss of any of it while adding the other reagents.

Generally glass or porcelain vessels are used, but because of their fragility it is better to use materials less easily broken. Larger quantities of neutral or almost neutral liquids are evaporated in enamelled dishes. These may also be used for zinc chloride melts, though copper dishes are also frequently used, as well as copper flasks, retorts, etc., all of which are very useful. The retort of the form illustrated (fig. 2) may be purchased in sizes from 0.25 liter up. Sulfonations are carried out in acid-resistant, that is high silicon, cast iron.

Since glass is strongly attacked by hot potash and soda lyes and since these bump badly in glass, experience has shown it is best to work with these in nickel vessels. In complicated cases a cover with two openings may be luted on a nickel crucible. A nickel tube closed at the lower end and reaching almost to the bottom of the crucible is sealed into the narrower opening. A thermometer is placed in the tube with a little paraffin to determine the temperature. In this way the thermometer is protected from the action of the lye. To the second opening is fastened a tube about 15 cm. long, which is wide enough so that the end of a reflux condenser, or even a stirrer may be introduced through the cork which closes it. With a tube of this length the boiling lye does not spatter on the cork.

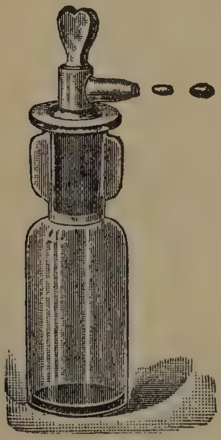

FIG. 1. DROPPING BOTTLE

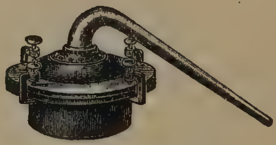

FIG. 2. COPPER RETORT

EXTRACTION

Extraction serves to transfer substances which are dissolved or suspended in one liquid to another which is not miscible with the first liquid, by shaking them with each other.

Improvement of extraction media by addition of other materials

The addition of many materials greatly improves the usefulness of extraction media, particularly of amyl alcohol. Willstätter made this important observation.[1] He found that dyes of all kinds, for example fuchsine, or the coloring matter of the red beet, which by themselves could not be extracted, went completely into the ether layer, when picric acid was added to their aqueous solutions. Dichlorpicric acid is better still, and the best extraction medium in such cases is not ether, but a mixture of 2 parts of amyl alcohol and one part of acetophenone, which, under these conditions, takes up quantitatively some of the natural monoglucosidic dyes.

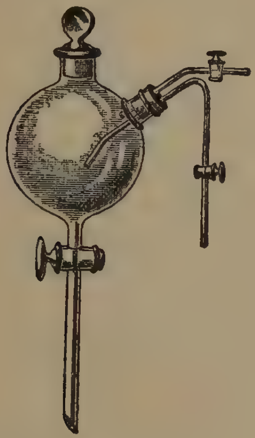

FIG. 3. SEPARATORY FUNNEL (BOLLAND)

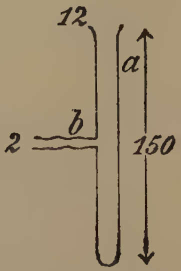

FIG. 4. SMALL FORM OF SEPARATORY FUNNEL (DOHT)

The separatory funnel

In most cases a separatory funnel provided with a delivery stopcock serves for the shaking together and subsequent separation of the two liquids. Schiff[2] recommends the substitution of a cylinder 400 mm. long and 60 or 30 mm. diameter, provided with a stop cock and stopper. In this, many chemical operations besides shaking out may be accomplished, and it also permits of the exact determination of the relation between the liquid to be extracted and the extraction medium. The writer determines this relation by measuring the two liquids in an ordinary graduated cylinder and then pouring them into the separatory funnel, thus avoiding the necessity of a special apparatus.

---

[1] Willstätter, R., and Schudel, G. Z., *Ber.*, **51**, 782 (1918).

Bolland[3] pointed out the need for a separatory funnel which would permit the renewal of the upper layer without first removing the lower layer from the funnel. His device (fig. 3) permits this renewal at any level of the funnel, saving time and trouble, especially during repeated extractions.

Doht[4] recommends the apparatus in Fig. 4 for shaking out small quantities of liquid. This is easily made from two glass tubes. For extracting with ether, for example, the small tube (*a*) is filled with the liquid to be extracted as up to the side tube (*b*); (*b*) is closed with the middle finger of the right hand and ether poured upon the lower slolution; (*a*) is then closed with the thumb of the same hand, and the apparatus thoroughly shaken. The ether is run off through the side tube after the layers have separated.

For a separatory funnel without a stop cock Kahlbaum's[5] dropping funnel is used. Holde[6] describes a usable substitute for large separatory funnels.[7]

For the extraction of small quantities of liquids there is also an

[2] Schiff, H., *Ann.*, **261**, 255 (1891).

[3] Bolland, A., *Ch. Zt.*, **35**, 373 (1911).

[4] Doht, R., *Ch. Zt.*, **29**, 309 (1905).

[5] Kahlbaum, George W. A., *Ber.*, **32**, 509 (1899).

[6] Holde, D., *Z. anal. Ch.*, **34**, 54 (1895).

[7] For the extraction of relatively large volumes (2 to 6 liters) of liquid, the operation may be satisfactorily carried out in a narrow-mouth stoppered bottle of suitable size (1 or 2 gallons capacity); the shaking is done by hand, and after settling, the watery layer is removed nearly completely by means of a siphon. The bulk of the lighter liquid may then be decanted, and the remaining small quantities of liquid separated in a small separatory funnel. When still larger volumes of liquid have to be extracted, a wide-mouth bottle is employed and the agitation effected by means of a mechanical stirrer. —H. T. C.

entirely different type of substitute for the separatory funnel. This is of special value in quantitative work. In such cases automatic extraction devices are used, which permit the liquid to be extracted to be traversed as often, and as long as possible by the warm extraction medium which is returned from a condenser. Partheil[8] states that although 100 parts of ether dissolve only 0.0077 parts boric acid, the latter may be extracted quantitatively on a technical scale if a stream of ether is allowed to flow through the acid solution. Laboratory extraction apparatus will be discussed later under the heading "Extraction."

Extraction media and the treatment of liquids and masses to be extracted

In practically all cases the following liquids are used for extracting: Ether, amyl alcohol, acetophenone, benzene, chloroform, ethyl acetate, petroleum ether, petroleum, phenol, pyridine, carbon bisulfide, sulphur dioxide; toluene.

Ordinary alcohol is frequently useful for shaking out aqueous solutions saturated with potassium carbonate. More details concerning these extraction media as to their purity, etc., will be found under the heading "Crystallization."

Furthermore, acids dissolved in solvents insoluble in water, such as benzene, may be shaken out with aqueous alkalies; dissolved bases or ketones (see below) with aqueous acids, that is, in such cases, they are transferred in combined form into the aqueous solutions. This will be discussed later.

The relative solubility of the material in the liquid from which it is to be extracted, which is usually an aqueous solution, and in the extraction medium determines how often the shaking out is to be repeated. Herb[9] extracted an acidified solution of tetrahydroterephthalic acid 30 times with ether to accomplish as nearly as possible a quantitative removal. In general it is well to determine whether profitable quantities are still being taken up by evaporating a test portion of the last extract on a watch glass.

When compounds are extracted from aqueous solutions with difficulty, it is often advantageous, before extraction, to evaporate the water solutions as far as possible if they will permit it, to diminish the quantity of extraction medium required. For such cases, the writer recommends a method which is almost always applicable and is more convenient for facilitating the extraction, particularly, of large quantities of liquid. This consists in saturating the liquid to be extracted with a readily soluble salt such as sodium chloride or magnesium sulfate,[10] or in certain cases with sodium hydroxide.

---

[8] Partheil, A., and Rose, J., German patent 136181 (1901); *Chem. Zentralblatt*, **73**, II, 1286 (1902); see also Partheil, A., and Rose, J., *Ber.*, **34**, 3611 (1901).

[9] Herb, J., *Ann.*, **258**, 46 (1890).

According to Herz[11] water takes up the following quantities of liquids when shaken with it:

	per cent
Ether	8.1
Amyl alcohol	3.3
Chloroform	0.4
Ligroin (specific gravity 0.6646)	0.34
Carbon bisulfide	0.17
Benzene	0.08

Ethyl acetate is also practically insoluble in water. Since many substances are much more soluble in it than in ether which is commonly used, it often offers considerable advantage over the latter in saving both time and material. In contrast to ether it can be recovered practically quantitatively by subsequent distillation from a water bath. This compensates for its higher price.

If the liquid to be extracted is viscous, or if solid particles are floating in it which may clog the stop cock, it is better to shake the liquids in a thick walled flask; pour off the clear layer after settling, and then finally transfer the whole to a separatory funnel.

Cocaine is obtained from the dried leaves of *Erythroxlyon coca*, a plant native to and cultivated in the interiors of Peru and Bolivia. When the medicinal value of cocaine was first recognized it was customary to send the dried leaves to Europe to be worked up. Because of a kind of putrescence, during the long voyage the cocaine content, originally 0.3 to 0.6 per cent, completely disappeared. It thus became necessary to extract the cocaine from the leaves as efficiently as possible on the spot and to completely purify it later in Europe. A maximum of 6 kgm. of crude cocaine was transported in place of 1000 kgm. of leaves. Pfeifer carried out this extraction by shaking the ground coca leaves for two hours in a closed vessel with dilute sodium hydroxide and petroleum. The sodium hydroxide, a strong alkali, liberates the cocaine, the alkaloid, from its compounds and the latter then dissolves in the petroleum. The petroleum is then separated from the aqueous suspension of the leaves and treated with hydrochloric acid, thus forming cocaine hydrochloride, insoluble in petroleum.

---

[10] Goering, Th., German patent 28064 (1883); *Ber.*, **17**, R, 394 (1884).

[11] Herz, W., *Ber.*, **31**, 2670 (1898).

In this way alkaloids may be extracted even from woods and similar materials. Salzberger[12] obtained a mixture easily extracted with ether by mixing 1 kgm. of medium fine root and 300 grams of barium hydroxide and adding 500 cc. of water. Using 5 kgm. of ether to 1 kgm. of roots the extraction was almost complete after shaking out three times.

After Baeyer[13] had shown that ketones react like bases, Weissgerber found that they may be extracted from solvents insoluble in water with the aid of dilute acids, just as are the bases. In particular he worked up crude benzene for its ketone content. This method of obtaining ketones may, under other conditions, also serve to separate them. It permits the working up of large quantities without demanding inconvenient apparatus. In one instance, 1000 kgm. of heavy benzene was extracted with 4 per cent sulfuric acid (60°Be.) More concentrated acid cannot be used because it greatly resinifies the unsaturated substances in the crude benzene. After the extraction, the sulfuric acid was diluted with water and the dissolved ketones blown out by a current of steam. In this way, 700 cc. of crude oil was obtained.

Extraction of liquids which form emulsions

If the liquid emulsifies when shaken, so that it does not separate again into two layers, it may often be made to do so by the addition of more solvent or of more water, as determined by a trial in a test tube. In cases in which ether causes the emulsification, the addition of alcohol often helps and the clear mixture of alcohol and ether soon floats above. It has been the writer's general experience that alcoholic ether is to be preferred, in many cases, to non-alcoholic for extraction.[14]

---

[12] Salzberger, G., *Arch. Pharm.*, **228**, 466 (1890).

[13] Baeyer, Adolf, and Villiger, Victor, *Ber.*, **34**, 2684 (1901).

[14] Salkowski, E., and H., *Z. physiol. Ch.*, **7**, 162 (1882).

Schröder[15] states that the addition of sodium chloride or ammonium sulfate[16] to the aqueous solution, facilitates the separation of the layers when shaking out with ethyl acetate. Others recommend calcium chloride for this purpose.[17]

In working with fats and oils very persistent emulsions are often formed between the fats and fatty acids and the aqueous liquids used for their purification or other purposes. Rost[18] lays the blame for these on the albumin and cell walls which are present to a greater or lesser extent in the vegetable and animal fats. The albumin or cell structures are quickly coagulated by formaldehyde and its polymers. Even with the most persistent emulsions, the addition of 0.3 per cent formaldehyde suffices, as a rule, to bring about a rapid and smooth separation. Strangely enough, the addition of ether, on the other hand, often breaks aqueous emulsions. Krämer and Spilker[19] found that synthetic lubricants, like lubricants in general, easily formed emulsions when washed with water. These emulsions did not break if kept lukewarm for days; but were easily broken by the addition of ether.

The following shows how it is possible to extract directly organic compounds from even the very strongest acids in which they are dissolved. The nitroglycerine which remains behind in the nitrating acids of the explosive factories is recovered by first shaking it out with chloroform. The nitroglycerine chloroform solution, after separation from the acids, is treated with paraffin oil, and the nitroglycerine, which is not soluble in the mixture of paraffin oil and chloroform, separates. The separation is so complete that the chloroform paraffin mixture may be subsequently separated into its components by distillation. The nitroglycerine residues[20] in the nitrating acids were a constant source of danger which has been eliminated by this process.

---

[15] Schröder, W. von, *Z. physiol. Ch.*, **3**, 325 (1879).

[16] Feist, F., *Ber.*, **28**, 740 (1895).

[17] The presence in the liquid of colloidal particles often causes the formation of a viscous, semi-solid layer at the interface of the two liquids, which prevents complete separation. It will be found that the volume of this semi-solid layer can be progressively decreased by alternately drawing off the clear portion of the heavier liquid and decanting as much of the lighter liquid as possible. When this process is no longer profitable, the interface can be cleared by filtering with suction, employing a soft filter paper previously moistened with water.—H. T. C.

[18] Rost, A., German patent 251848 (1911); *Chem. Zentr.*, **83**, II, 1508 (1912).

[19] Krämer, G., and Spilker, A., *Ber.*, **24**, 2788 (1891).

There are, however, liquids which cannot be shaken out by any process, because of emulsification. In this class are most animal and human urines, which resist extraction either directly or after the addition of acid or alkali. Slightly acidified rabbit urine often solidifies to a jelly when shaken with ether, for example.

Consequently there has been developed in the biochemical laboratories a very definite method of treating urines, which, *mutatis mutandis*, the writer has found to be useful in purely chemical laboratories in dealing with liquids prone to form emulsions.

Water is removed from the urine by evaporation on the water bath until a sirupy residue is left, that is, almost to dryness, and the residue is extracted several times with boiling alcohol in the following way: Alcohol is poured on the residue and allowed to come to a boil in the porcelain dish on the water bath and then poured off into a beaker. This extraction is usually repeated four times and the quantity of the alcoholic extract should be about 1½ times the original volume of the urine. (The insoluble portion consists almost entirely of the inorganic salts of the urine.) The alcoholic extract, after standing twenty-four hours has deposited the impurities sufficiently so that it may be filtered easily, indeed the urine of rabbits deposits its resinous materials so firmly on the walls of the vessel that the clear alcoholic solution may be poured off directly. The alcoholic extract is now evaporated as far as possible; the residue stirred with water and this aqueous magma, either as it is, or after acidification, or else after the addition of alkali, or even in each of these three conditions, may then be shaken out with ether, ethyl acetate, amyl alcohol, etc., without danger of emulsification. In one of these solvents will usually be found those substances which are formed in the body of the animal after treatment with drugs or chemicals, and their recovery is often a matter of interest.

Ragnar Berg[21] extracted beeswax with alcohol, evaporated the filtrate to dryness, redissolved it in petroleum ether, or ether, or chloroform and filtered the solution again. On attempting to shake out the free acids from these solutions with soda lye, emulsions were formed which could not be broken, even though the most dilute lyes were used. Successfully using his previous observations as a starting point, he added acetone until no more turbidity ensued after lengthy standing and renewed additions of acetone, and then filtered off the precipitate consisting of alkali, alkali carbonate and soap. The acetone was evaporated and the aqueous residue was easily extracted with ether.

---

[20] Sprengstoffwerke R. Nahnsen & Co.—Akt. ges. Hamburg, German patent 250444 (1910); *Chem. Zeit.; Chem. Techn. Repertorium*, **36**, 530 (1912).

[21] Berg, Ragnar, *Ch. Zt.*, **32**, 777 (1908).

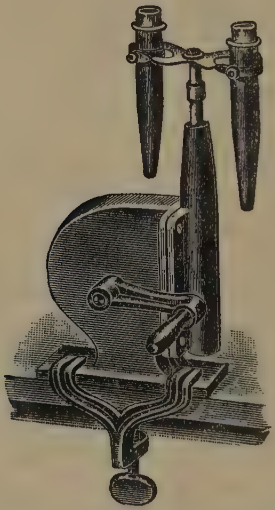

Fig. 5. Laboratory Centrifuge

Another and universally successful method of dealing with emulsions is centrifuging. Centrifugal force ordinarily accomplishes a rapid separation of the two liquids corresponding to their densities. In this way it is possible to break even the emulsion obtained by violently shaking urine with amyl alcohol in a test tube. Otherwise, the emulsion is stable for weeks.

Porcelain centrifuges, both hand and motor driven, are now available. Richards[22] has given an excellent discussion of the use of centrifuges in the laboratory which is too extensive to repeat here.

Heating the ordinary centrifuges is out of the question. Rivat[23] has constructed an electrically driven centrifuge which carries four insulated tubes on an electrically driven sling, and these may be heated electrically by means of equal resistances.

---

[22] Richards, T. W., *Ch. Zt.*, **31**, 1251 (1907); *Ber.*, **40**, 2771 (1907).

[23] Rivat, G., *Ch. Zt.*, **37**, 1506 (1913).

Extraction of warm liquids and their evaporation

Obviously, warm liquids may be more rapidly extracted with warm ether, for example, because of its greater solvent power, than is possible with cold liquids. This process,[24] which has been recommended for technical use for the extraction with ether of alkaline liquids at 35° in pressure flasks, cannot be used in the laboratory for lack of suitable apparatus and because of the great fire hazard. Amyl or butyl alcohol may be used if warm liquids are to be shaken out in the laboratory. Liquids which have been extracted with ether dissolve so much of it that they should never be directly evaporated on a water bath under the hoods because of the inflammability of warm ether. The hood is soon filled with ether vapors and violent explosions usually follow such carelessness. If such liquids are to be evaporated, a stream of air should be passed through them until it has carried off the ether, before they are placed on the water bath. This does not consume much time. If the quantity of liquid is small it may be placed on a boiling water bath the flame under which has been extinguished. The heat is sufficient to evaporate this small quantity of ether and the real evaporation commences without danger.

Further general statements

If acid aqueous solutions containing hydrochloric or acetic acids have been shaken out, and the extraction liquid is acid, where this reaction is not supposed to be due to the organic compound extracted, potassium hydroxide is added either as solid or a few drops of solution. It is better to use sodium or potassium carbonate or bicarbonate, or else calcium carbonate.[25] If organic acids have gone into the ether, any hydrochloric or acetic acid present with them is removed by shaking the ether solution with much water. This removes the hydrochloric[26] or acetic acid.[27] If the ether solution is now shaken with dilute sodium carbonate solution, an aqueous solution of the sodium salt of the desired organic acid, practically free from sodium chloride or acetate, is obtained. It would be much better to acidify the original solution, if necessary, with tartaric and similar acids because these do not go into the ether.[28]

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[24] Ch. Fab. E. Schering, German patent 95622 (1896); Fr. V, 780.

[25] Tcherniac, J., *Ber.*, **25**, 3649 (1892).

[26] Liebermann, C., and Scholz, W., *Ber.*, **25**, 950 (1892).

[27] Liebermann, C., and Hartmann, A., *Ber.*, **24**, 2583 (1891).

A fuller discussion of methods of avoiding bumping of the liquids to be distilled will be found under the heading "Delayed Boiling of Liquids."

If ether extracts will not permit the removal of the ether by distillation, either because of chemical reasons or danger of explosion, it may be removed by a strong current of air. If that is not permissible, it is allowed to evaporate spontaneously or in a vacuum over sulfuric acid and paraffin.

If, for example, an oxidizing agent such as potassium ferricyanide is allowed to react on an alkaline solution of diazobenzene, the fourth possible nitro derivative of aniline results, namely that one in which the nitro group replaces a hydrogen atom of the amino group. Ether extracts this from the reaction liquid and it remains as crystals when the ether is evaporated. These crystals explode, however, if the temperature of the water bath rises to about 70°. It is necessary to allow the last portion of the ether to evaporate spontaneously to avoid an explosion.

It should be noted that explosions occasionally occur when ether is distilled by itself. This is ascribed to an abnormally high content of hydrogen peroxide or ethyl peroxide.[29] Such explosions have occurred when evaporating the last portions of ethereal solutions in an open dish at about 60°. Schär[30] has written extensively concerning this. Börrigter[31] states that iodine is liberated from potassium iodide by ether if the latter contains hydrogen peroxide, as it usually does. Ditz's[32] test is much more sensitive. The blue solution of the so-called potassium cobaltate is decolorized by the hydrogen peroxide contained in ether. Indeed, the oxidizing materials present in ether may lead directly to oxidations. Rossolimo[33] states that when he extracted an aqueous solution of caffeiniod-alkylate with impure ether, he observed the liberation of iodine, which in its turn immediately caused the separation of crystalline caffein periodide, insoluble in water and ether. (Further details concerning ether will be found under the heading "Solvents and Diluents.")

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[28] Dreser, H., *Arch. Pathol. and Pharm.*, **26**, 241 (1890).

[29] Cleve, P. T., *Proc. Chem. Soc.*, page 15, (1891); *Ber.*, **25**, R, 745 (1892); Ditz, H., *Ber.*, **38**, 1409 (1905).

[30] Schär, E., *Arch. Pharm.*, **225**, 623 (1887); Brühl, J., *Ber.*, **28**, 2858 (1895); Richter, M., *Chem. Industrie*, **30**, 300 and 417 (1907).

[31] Börrigter, B., *Z. anal. Ch.*, **25**, 98 (1886).

[32] Ditz, Hugo, *Ber.*, **38**, 1410 (1905).

According to Börrigter, ether treated for a long time with solid potassium hydroxide no longer shows the iodine reaction, nor does it change the cobalt solution.[34] Since it then no longer colors sticks of potassium hydroxide yellowish brown, it is, after this treatment, free from aldehyde which causes this coloration. He states that after long storage the peroxide content of ether is greater if kept in bottles with glass rather than with cork stoppers. The writer believes that the peroxide present in ether could be removed by shaking it with permanganate solution, since the latter reacts readily with peroxide. A further discussion of the characteristics of ether will be found under the heading "Crystallization."

If the large volumes of ether essential for extraction are used repeatedly with the same alkaloid, it is not distilled after each extraction, but is made fit for use again by removing the alkaloid by shaking it with a dilute acid, such as sulfuric. Finally the acid solution is made alkaline and the alkaloid is then extracted from it with fresh ether which is then distilled off, leaving the alkaloid in a fairly pure condition. What has been said here regarding alkaloids can, of course, be applied to all alkaline and acid materials.

If the product which has gone into the ether is very volatile with ether vapors, as Bamberger[35] found true of decahydroquinoline, the ether is not distilled directly, but a suitable still head (see Distillation) must be used.

Salkowski[36] found that ether takes up traces of sodium salts of certain volatile organic acids.

Since it may happen that the extraction medium used, say ether, cannot be separated by distillation from the material which has gone into it, because the boiling points of the two substances lie too close together, a method of separating ethyl bromide and ether, other than by distillation, is given. The procedure in each case must, of course, be governed by the behavior of the substance dissolved in the extraction medium. The following method may be used to a certain extent as a starting point.

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[33] Rossolimo, A. J., *Ber.*, **38**, 774 (1905); see also Decker, H., *Ber.*, **36**, 1212 (1903).

[34] Ditz, Hugo, *Ch. Zt.*, **29**, 705 (1905).

[35] Bamberger, Eug., and Lengfeld, F., *Ber.*, **23**, 1144 (1890).

[36] Salkowski, E., *Z. physiol. Ch.*, **9**, 493 (1885).

If ethyl bromide is prepared by the action of a bromide on ethyl sulfuric acid, there is obtained, in addition to the ethyl bromide, 7 to 9 per cent of ethyl ether which cannot be separated from the ethyl bromide by fractional distillation, since their boiling points are practically the same. Pure ethyl bromide, free from ethyl ether, is absolutely essential for many purposes. This is true, for example, of the preparation of nitrophenetole, $C_2H_5O \cdot C_6H_4 \cdot NO_2$, from sodium nitrophenate and ethyl bromide, since the yield is markedly reduced if the ethyl bromide contains ether. Riedel[37] achieves this necessary complete separation of ether and ethyl bromide by shaking the mixture with sulfuric acid. This dissolves the ether with evolution of heat without influencing the ethyl bromide. A thick walled, closed glass vessel or a reflux condenser is used because of the heat developed. The weight of sulfuric acid needed is about that of the ethyl bromide. The separation then follows in a separatory funnel.[38]

The writer pointed out long ago that the purification of anthracene with liquid sulfur dioxide represents a general procedure worthy of note. In 1912 Edeleanu[39] showed that distilled petroleum could be purified better by shaking it with sulfurous acid than with sulfuric. The latter destroys the harmful materials present and they are lost, whereas when they are extracted with liquid sulfur dioxide they dissolve in it and are recovered as oils, when it is evaporated. The extensive work of Engler and Ubbelohde[40] shows that these oils are useful for many purposes. It may be that the extraction of non-aqueous liquids with liquid sulfur dioxide in the laboratory will lead to the isolation of substances which have never been obtained as solids.

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[37] Riedel, J. D., German patent 52982 (1889); Fr. II, 551.

[38] A good way to accomplish this is to place the ethyl bromide in a separatory funnel, add a very small amount of sulphuric acid, shake and draw off the acid. Continue shaking with small amounts of acid as long as any action is apparent.

[39] Edeleanu (Disconto Gesellschaft), German patent 216459; *Chem. Zentr.*, 81, I, 70 (1910).

[40] Engler, C., and Ubbelohde, L., *Z. angew. Ch.*, **26**, 177 (1913).

The behavior, nature and usefulness of liquids used for extraction

As might be expected, the solubility of materials in the extraction medium differs widely; thus one part of hippuric acid at 20 to 25° dissolves in 200 to 270 parts of ether saturated with water, but in only 16 to 22 parts of ethyl acetate. Bunge and Schmiedeberg have shown that hippuric acid may be separated quantitatively from benzoic acid in this way. If an aqueous solution of these two acids is shaken with petroleum ether, all of the benzoic acid, but not a trace of the hippuric acid, is extracted.[41] It has been shown that solanin[42] may be extracted from alkaline solution by amyl alcohol only, but not by ether, benzene, chloroform, ethyl acetate or petroleum ether. The fact that ions do not pass from water into other solvents makes possible numerous exact methods of separation.

The quality of the commercial grades of the liquids suitable for extraction is often so poor that the impurities may exert a very deleterious action. This is especially true of amyl alcohol, the purification of which will be discussed later in detail, because it is an extraction medium adapted to many purposes. It is seldom used for recrystallization; while the other liquids considered here are more frequently used for this purpose than for extraction. The impurities to be guarded against in these other liquids will be discussed under the heading "Crystallization," where they will be more fully considered.

Commercial amyl alcohol is especially apt to contain materials that resinify during the extraction of either acid or alkaline liquids, and the resins[43] thus formed may considerably increase the difficulty of purifying the materials extracted by the alcohol. Udranski[44] states that it is chiefly furfurol which gives the alcohol this undesirable characteristic. Konek[45] observed a continuous current of a basic gas issuing from the condenser when he boiled supposedly pure amyl alcohol with sodium. When he passed this gas through hydrochloric acid he could obtain only 0.1 gram of a hydrochloride from 800 grams of amyl alcohol. Bamberger and Einhorn[46] investigated this question thoroughly in 1897. They found the basic content of technically "purest" amyl alcohol to vary greatly with its source. While they worked for years with a product containing no bases, or only traces, they were able to extract approximately 0.1 per cent of basic material from the amyl alcohol obtained at other times from different sources. Among these basic substances they proved the presence of pyridine and particularly 2, 5-dimethylpyrazine:

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[41] Bunge, G., and Schmiedeberg, O., *Arch. Path.*, **6**, 237 (1877).

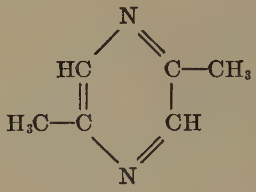
[42] Rentelen, C., *Z. anal. Ch.*, **21**, 620 (1882).

[43] Siegfeld, M., *Zeit. angew. Chem.*, **16**, 1217 (1903).

[44] Udranski, L. von, *Z. physiol. Ch.*, **13**, 248 (1889).

[45] Konek, von Norwall, Fr., *Ber.*, **28**, 1638 (1895).

[46] Bamberger, Eug., and Einhorn, Alfr., *Ber.*, **30**, 224 (1897).



A mixture of the homologues of these substances was also present. The occurrence of nitrogenous substances in amyl alcohol is no longer surprising. In a remarkable piece of work in 1905, Ehrlich[47] showed that the fusel oils are formed as follows in the fermenting liquid: the "amino acids" as well as the sugar, which the yeast converts into ethyl alcohol and carbon dioxide, are changed into "higher alcohols." The mixture of the two fermentation amyl alcohols is derived from leucine, *i.e.*, from amino-caproic acid.

The alcohol is purified by converting it into the potassium salt of amylsulfuric acid, and this salt is purified by several recrystallizations. The salt is then decomposed by warming it on the water bath for five hours with 10 per cent sulfuric acid:

$$C_5H_{11}\cdot O\cdot SO_3H + H_2O = C_5H_{11}OH + H_2SO_4,$$

and the amyl alcohol drawn off, the acid removed from it by shaking with calcium carbonate, and then steam distilled. The product thus obtained may be used for extraction.

If a still purer amyl alcohol is desired, it is necessary to use Marckwald's process[48] which goes through acid amyl-nitrophthalate. This was the first method to make possible the preparation of a perfectly uniform active amyl alcohol, and gives a chemically pure product.

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[47] Ehrlich, Felix, *Z. f. Zuckerind.*, **55**, 539 (1905), and **57**, 631 (1907); *Ber.*, **40**, 1027 (1907).

[48] Marckwald, W., and McKenzie, Alex., *Ber.*, **34**, 485 (1901).

Amyl alcohol is much used in the recovery of alkaloids, particularly of the small quantities dealt with in cases of poisoning. Uslar and Erdmann[49] first showed that free plant bases are very soluble in it, especially if it is used hot, and since it boils at 132°, aqueous solutions may be treated with it without special precautions, in contrast to ether, carbon bisulfide, etc. On the other hand, they showed that an amyl alcoholic solution does not give up its alkaloid to even large quantities of water, provided the latter is alkaline. Since the hydrochlorides of the alkaloids are difficultly soluble in amyl alcohol, the plant bases may be easily and completely removed from it by simply shaking with very dilute hydrochloric acid. Thus its aid is a great convenience in their preparation in a pure condition. (See the preparation of cocaine previously discussed.)

If the material which has gone into the amyl alcohol cannot be recovered by shaking with acid or alkaline water, the alcohol is distilled off with steam, or from an oil or metal bath. The latter operation may be carried out in vacuo.[50]

Phenol is used less than it deserves to be as an extraction medium in laboratories, but it plays a great rôle in technical practice.

Bernthsen[51] states that methylene red is obtained from methylene blue mother liquors by extracting it with phenol. It is then precipitated as a crystalline mass from the phenol solution by the addition of alcohol and ether, and may be purified by several recrystallizations from alcohol.

Diazo bodies[52] may also be extracted with phenol. If a solution of 7.5 kgm. of sodium nitrite in 15 liters of water is added to 10 kgm. of aniline dissolved in 30 kgm. of hydrochloric acid diluted with 100 liters of water, the resulting diazobenzene hydrochloride may be shaken out with phenol. For the first extraction 30 kgm. of phenol are used, for the next three, 10 kgm. each. These solutions of diazo bodies are stable for only a few days. After this time, or immediately upon warming, changes occur with evolution of nitrogen.

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[49] Uslar, L., and Erdmann, J., *Ann.*, **120**, 121 (1861).

[50] Klingemann, F., and Laycock, W. F., *Ber.*, **24**, 513 (1891).

[51] Bernthsen, A., *Ann.*, **251**, 5 (1889).

[52] Hirsch, R., German patent 58001 (1890); Fr. III, 51.

According to Cremer[53] pyridine may be used for the extraction of urine. By this method he succeeds in removing much colouring matter from the urine; a fact of interest sometimes, since the other methods usually cause greater changes.

Ethyl alcohol. Up to this time the writer appears to have been the only one to use ethyl alcohol as an extraction medium, although it alone, in contrast to all the usual ones, takes up the potassium salts of organic acids with the greatest ease from aqueous solutions to which much potash has been added. The writer[54] boiled human gall for twenty-four hours with a considerable excess of 6 per cent potash lye in order to split off the glycocoll and taurin from the conjugated gall acids. The free alkali in the liquid was neutralized by a current of carbon dioxide and the solution evaporated on the water bath. Three extractions with 90 per cent alcohol in a separatory funnel quantitatively removed the potassium salts of the organic acids from the viscous residue. This is evident since the residue, if diluted and treated with acid, gives not a trace of precipitate of cholic acid, fatty acids, etc., all of which are dissolved in the alcohol as potassium salts.

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[53] Cremer, Max, *Z. Biol.*, **36**, 124 (1898).

[54] Lassar-Cohn, *Ber.*, **27**, 1340 (1894).

CHAPTER II

BATHS

WATER BATHS

In a private communication Emil Fischer stated, that in general, it is preferable to evaporate aqueous solutions in flasks with side tubes, rather than in open dishes on the water bath. The side tube leads into a second similar flask acting as a receiver and its side tube is connected with the air pump (see the heading "Distillation under Reduced Pressure"). The evaporation proceeds much more rapidly in vacuo than on the water bath and this arrangement is very generally used in many laboratories.

Baths are used to heat bodies more uniformly than is possible over a free flame. They thus serve to exclude the direct action of the flame so that an excessive heating of the substances and breaking of the vessels may be avoided as much as possible.

Water baths, sodium chloride, potassium nitrate, and calcium chloride baths are used. In time, the latter especially greatly corrodes copper, so that enameled ware should be used, at least with such solutions. According to Gerlach,[1] saturated solutions of sodium chloride boil at 108°, saturated sodium nitrate solutions at 120° and Legrand[2] gives 180° as the boiling point of saturated calcium chloride solutions. Ordinary olive oil[3] has been recommended for baths between 50° and 220°, and mixtures of molten salts for higher temperatures. For example, an equal molar mixture of KNO_3 and $NaNO_3$ melts at 219°; no vapors are evolved nor are there any other disagreeable features. The baths may be heated above 650° in an iron vessel. (See below.)

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[1] Gerlach, G., *Z. anal. Ch.*, **26**, 426 (1887).

[2] Legrand, J., *Ann.*, **17**, 34 (1836).

[3] Lubricating oil of high flash-point forms a very satisfactory bath. The "Navy Valve Mineral Oil" manufactured by the Vacuum Oil Company is particularly recommended. It smokes only slightly at 200° and not at all at 190°. —H. T. C.

Mixtures for cooling baths in which low temperatures are to be maintained will be discussed under the heading "Crystallization."

Water baths are provided with a connection with the water system, if available, in order to maintain a constant level and to prevent their going dry.

For many years the writer used five connecting water baths whose arrangement is clear from figure 6. These are placed in the back wall of a hood and filled from a common overflow A. In spite of hard usage, a quarterly cleaning is sufficient to prevent any clogging by Königsberg tap water.

In general the temperature of a bath should be 20 to 30° higher than the boiling points of the liquids to be heated in it. This accounts for the practice of placing a flask from which alcohol is to be distilled in the boiling water of the bath, since satisfactorily rapid distillation can not be accomplished by placing it on the bath, that is, in the vapors. On the other hand, flasks containing ether are always placed on the bath. Ethyl acetate must be placed in the boiling water or the distillation will be unreasonably slow. It is well to place a cloth in the water of such baths to avoid breaking the flask on the hard bottom.

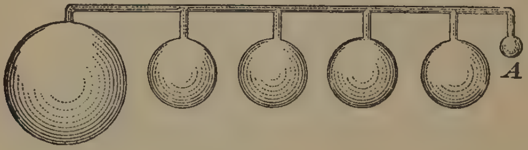

Fig. 6. Water-Bath Battery, Top View (Lassar-Cohn)

If ether and similar inflammable materials are to be evaporated on the water bath, the flame which heats it should be surrounded by a fine mesh gauze to prevent ignition (see fig. 7). But it is generally known that fires do occur because of the breaking of flasks during the boiling and distillation of inflammable liquids, in spite of the use of safety water baths. There is no fire danger if the steam bath of Kumm[4] is used, where steam is substituted for the flame. Its funnel shape has the further advantage that all sized flasks fit in the bath and may be used without further change. The steam enters at the lower end of the funnel, circulates around the flask and heats it

[4] Kumm, Aug., *Ch. Zt.*, **34**, 801 (1910).

uniformly. The condensate flows out of the bent exit tube. The use of this steam bath permits the distillation of even large quantities of liquid without fear of fire (fig. 8).

If it is desired to heat aqueous solutions to 100° in the water bath without evaporating the water from them, sealed tubes (though very inconvenient), or the capped bottles commonly employed for beer or seltzer, may be used. For quantitative work, Küster's[5] procedure, which he proposed for the quantitative estimation of aromatic hydrocarbons by means of aqueous picric acid solution, is preferable. A flask, whose walls are not too thin, is closed with a good rubber stopper through whose opening passes a tube about 7 cm. long which can be moved without difficulty and whose lower end is sealed. A small lateral hole is blown about 1.5 cm. above this end, through which the [illegible] may be evacuated if the tube is pushed down far enough. After the evacuation is completed, and while the pump is still working, the tube is raised until the sealed end is flush with the bottom of the cork thus interrupting the communication between the inside of the flask and the atmosphere. If everything fits well, and if the stopper and tube are moistened slightly when fitted together, the flask will hold a constant vacuum for days, so that it may be heated in the water bath, and no pressure will develop within it. After cooling, and before the flask is opened, air is admitted by pushing down the tube.

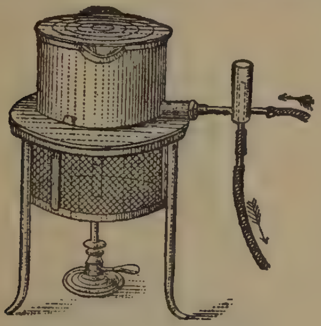

Fig. 7. Water-Bath with Protective Cover and Overflow

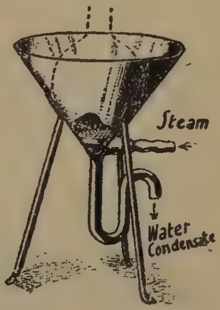

Fig. 8. Vapor-Bath (Kumm)

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[5] Küster, F. W., *Ber.*, **27**, 1102 (1894).

OIL BATHS, ETC., METAL BATHS

Toluene-, oil-, paraffin-, glycerine-, diphenylamine-[6] or sulfuric acid baths may be used for higher temperatures than can be obtained with water baths. Potassium sulfate may be added to sulfuric acid baths so that they may be used up to 360° (for details see the heading "Determination of Melting Points"); and diphenylamine baths to 310°. Glycerin baths remain transparent longer at 160 to 170° than oil or sulfuric acid baths.

If definite, constant higher temperatures are to be maintained for long periods in such baths, a regulator[7] must be used to control the gas flame, and the bath must be fitted with a mechanical stirrer. To prevent excessive cooling of the surface of the hot material, the bath must be provided with a cover having the necessary openings. Because of the high heat conductivity of the metals, such accessories are not necessary for metal baths, but a simple gas regulator is sufficient. The all-metal regulator proposed by Giroud has proved very valuable because of its simple construction and durability (fig. 9).

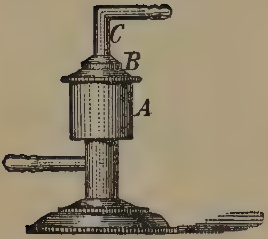

FIG. 9. GAS PRESSURE REGULATOR (GIROUD)

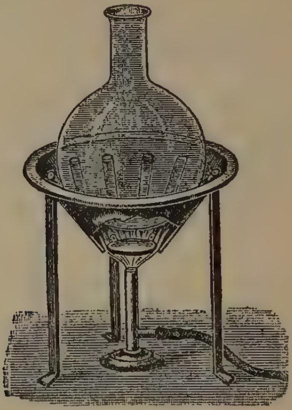

FIG. 10. BOILING FUNNEL (BABO)

Jorissen[8] has described a thermostat which can never cause a fire, since in it the use of rubber tubes, etc., is eliminated.

[6] Gabriel, S., and Leupold, E., *Ber.*, **31**, 1277 (1898).
[7] Knoevenagel, E., and Arndts, J., *Ber.*, **35**, 1987 (1902).
[8] Jorissen, W. P., *Z. angew. Ch.*, **26**, 637 (1913).

Metal baths are to be preferred to those mentioned above since they evolve no ill smelling or acrid vapors and it is not necessary to use them under hoods. They consist of alloys placed in rather flat cast iron vessels.

They may be used at comparatively low temperatures if they are made of Wood's[9] metal, (1 to 2 parts cadmium, 2 parts tin, 7 to 8 parts bismuth) melting at 71° or of Rose metal (2 parts bismuth, 1 part lead, 1 part tin) melting at 95°. On the other hand, these metallic mixtures may be heated almost to redness in cast iron vessels. For higher temperatures, and for reasons of economy, it is preferable to use a mixture of 1 part lead and 1 part tin, melting at 200°, or even pure lead which melts at 313°.

Smith and Davies[10] recommend coating the part of the flask which dips into the metal with lamp black to prevent the metal sticking to the flask when it is removed from the bath.

DOUBLE GAUZES, BOILING FUNNELS, DRY BATHS, AIR BATHS

Two gauzes laid upon each other may be used, in many cases, in place of the high temperature baths discussed below, since they permit much more rapid heating. Years of experience have shown the writer that such double gauzes distribute the heat of the flame so uniformly that even large beakers, which it is dangerous to heat over a single gauze, have never broken.

Babo boiling funnels may be recommended for heating flasks (fig. 10). The flasks stand in a sheet iron funnel whose walls are covered with strips of asbestos which hinder the breaking of the flask, and furnish a passage for the ascending gases from the flame. The bottom of the funnel is almost closed by a fitted sheet iron plate and the burner is placed below. The flasks are not touched by the flame itself but only by the current of hot air which ascends around the bottom plate.

Dry baths are dishes containing sifted cast iron chips. They may for instance be used with reflux condensers which are to be kept in action for days at a time, even though alcoholic or ether solutions are being boiled, because the refilling of water baths, even though they would answer this purpose, is eliminated. Graphite may be substituted for the cast iron chips or even sand, though it is not so good because it conducts heat so poorly. Consequently, the layer of sand in such baths should be very thin.

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[9] Buchner, Ed., and Witter, H., *Ber.*, **27**, 875 (1894).

[10] Smith, W., and Davies, G., *J. C. Soc.*, **37**, 416 (1880).

Air baths like that of Lothar Meyer,[11] through which a current of hot air circulates, may be used for many purposes.

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[11] Meyer, Lothar, *Ber.*, **22**, 879 (1889).

CHAPTER III

Distillation

SIMPLE DISTILLATION AND COOLING DEVICES

Haas[1] stated that expensive materials should be distilled from flasks of good quality, one third of whose volume is covered with a stout layer of closely adhering copper, 0.5 mm. thick. It is possible to heat these flasks over a free flame up to the melting point of tin, without danger of breakage.

When dealing with materials on which the alkalinity of the glass exerts a deleterious influence, Bloch[2] recommends passing a stream of dry hydrochloric acid gas through the assembled apparatus. The acid gas is displaced after some time and the harmful effect is no longer evident.

The fact that foam may be broken by strongly blowing on the walls of the vessel, led Fanto[3] to investigate whether a current of air or of an indifferent gas, directed on the surface of the boiling liquid would not have the same, or a better effect. The experiments showed that this means not only completely obviated all foaming, but did not in the least diminish the rate of distillation, since there was no objection to increasing the heating; so that from distillation flasks of the same size it was possible to distil more rapidly with a current of air than without one. It should be noted that a current of steam does not break foam. In this way, Fanto easily distilled aqueous and aqueous-alcoholic soap solutions. Of course the soap solution foamed badly while being heated to boiling, but a current of air caused the foaming to cease immediately. The destruction of the foam can only be explained by the sudden condensation of the vapor of the liquid which fills the bubbles. It should be observed that the stronger the current of gas, the more liquid is carried into the receiver as mist, but this may be avoided by the use of a suitable still head or a second and easy redistillation may be made. This will be discussed further under the heading "Delay in Boiling and Foaming over of Liquids."

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[1] Haas, *Ch. Zt.*, **37**, 1506 (1913).

[2] Bloch, Ignaz, and Höhn, Fritz, *Ber.*, **41**, 1972 (1908).

[3] Fanto, R., *Z. angew. Ch.*, **20**, 1233 (1907).

The purpose of distillation is the separation of volatile from non-volatile materials. Fractional distillation under closely maintained conditions serves to purify materials.[4] Liquids to be distilled are ordinarily heated in glass or metal retorts or flasks. Spasmodic boiling often occurs and at times the liquids tend to foam over. Other methods of combating this will be discussed under the heading "Delay in Boiling and Foaming Over of Boiling Liquids."

Retorts, which are usually preferable for liquids boiling above 200°, are connected with condensers by an adapter which keeps the gases passing over from undue contact with cork or rubber. If none of a solid is to stick in the neck of the retort it may be carefully slid into the bulb in one or more boats (fig. 11).[5]

The cooling device bearing Liebig's name is generally used in the laboratory to condense the products passing over during distillation. The counter current principle is used in it. Schelenz[6] has pointed out that the "Liebig Condenser" was not invented by Liebig but by Magellan about 1770.

If the connections on distilling apparatus cannot be made tight by organic material, plugs of asbestos—water glass, as recommended by Vorländer and Schilling,[7] may be used. For example, a retort may be connected with a receiver by a strip of thin asbestos paper 2.5 cm. wide fastened to the tube with syrupy water glass solution and then wound around until the stopper is thick enough; the end of the strip and the bandage are fastened with a little water glass. The plug is ready for use after drying in the air from ten to twenty minutes. It may be used repeatedly, inserted in the retort, and taken out, and forms a perfectly satisfactory seal, even for vacuum distillations, (see below). Hensgen[8] states that removable asbestos rings may be made by winding asbestos cord, moistened with a very thin solution of gypsum, around the proper sized tube, and then pressing moderately. Such rings hold together well when dried.

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[4] Special precautions for the preparation of pure distilled water may be found in *Untersuchungen über die chemischen Proportionen* by Stas, translated by Aronstein L., Leipzig 1867, p. 110. See also Mylius, F., and Foerster, F., *Ber.*, **24**, 1492 (1891).

[5] Zellner, H., German patent 271219; *Chem. Abstracts*, **8**, 2088 (1914).

[6] Schelenz, H., *Z. angew. Ch.*, **23**, 1978 (1910).

[7] Vorländer, D., and Schilling, R., *Ann.*, **310**, 372 (1900).

[8] Hensgen, C., *Ch. Zt.*, **17**, 395 (1893).

According to Kraze,[9] ordinary clay which need only be made into a plastic mass with water, is well suited for sealing connections on glass tubes, stopper openings, etc., in short, for all cases when paraffin or similar materials are often used. Because of its plasticity it may be easily shaped to any form and pressed into the finest crevices. For this purpose, the moist clay is best formed into pencil-like rods which are pressed around the connections to be closed. Clay has the advantage over other sealing materials of resisting heat better.

Other materials of this kind made of organic substances will be mentioned under "Vacuum Distillation and Sealing of Desiccators."

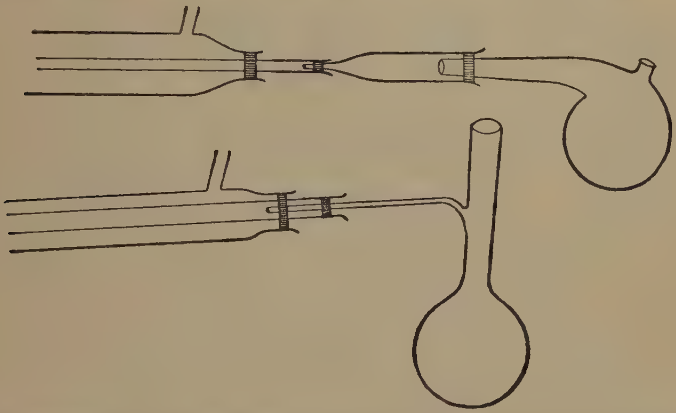

FIG. 11. METHOD OF CONNECTING RETORTS AND FLASKS WITH CONDENSERS

Flasks for distillation should have fused into them, if possible, a side tube bent upward as shown in figure 11, so they can be easily connected with the condenser. This upward bend, originated by the writer, prevents any liquid carelessly poured into the flask from running through the side tube.

The Claisen flask is a greatly improved form (fig. 12). When distilling liquids whose vapors attack cork or rubber, it is best to use these double necked distilling flasks, if apparatus with ground glass stoppers is not available. The neck carrying the thermometer and exit tube is so long that it can accomodate the whole thermometer, and the vapors can hardly reach the stopper. A plug of glass wool may serve as an additional protection for the stopper. See also under the heading "Delay in Boiling and Foaming Over of Liquids," where a distillation apparatus is described that thoroughly prevents foaming over by treatment with a current of carbon dioxide.

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[9] Kraze, F., *Ch. Zt.*, **32**, 819 (1908).

According to Reden,[10] most distilling flasks are difficult to clean and it is impossible to remove their contents quantitatively. These disadvantages are avoided by using conical flasks with hemispherical bottoms (fig. 13), in which all parts of the walls may be reached with a brush. (The Erlenmeyer flask with its straight sides has proved, of course, a very practicable substitute for flat bottom flasks, but it may not be evacuated as can the Reden flasks.)

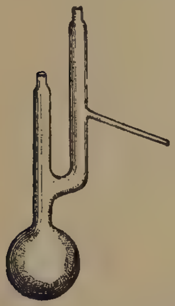

Fig. 12. Double Neck Distillation Flasks (Claisen)

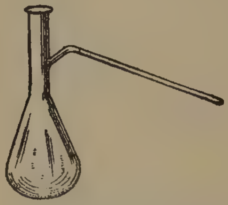

Fig. 13. Distillation Flask (Reden)

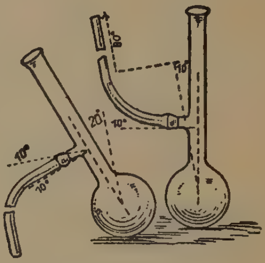

Fig. 14. Universal Flasks (Gabriel)

The universal flasks of Gabriel,[11] which have proved of practical value for various uses in the Chemical Institute of the University of Berlin, must be mentioned here. The round flask has, near the bottom of its neck, a projection extending upward about 10 degrees from the vertical. On this is fitted by a ground joint, a cooling tube bent almost at right angles, over which, for low boiling liquids, a Liebig condenser jacket may be pushed (fig. 14). The advantage of this construction is that the cooling tube may be adjusted to every desired position from vertically upward to vertically downward, by turning it on the ground surface. Thus the same flask may be used with a reflux condenser or for fractionation. Since these operations often follow each other when working with the same substance, there is no loss due to transfer. These flasks have the further advantage that the opening of the cooling tube may be adjusted at any desired height; gases are easily led into them, liquids dropped in, or solid materials added. In this last case, the neck is closed by a clean two hole asbestos stopper not very susceptible to attack.

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[10] Reden, U. von, *Ch. Zt.*, **38**, 20 (1914).

[11] Gabriel, Fritz, *Ch. Zt.*, **36**, 44 (1912).

The tube flasks of Müller are very useful. A tube, leading to the middle of the bottom, is sealed in the bulb. This device makes them particularly suitable for chlorinations, esterification in a current of HCl, and heating of reaction mixtures in various gases, since it is only necessary to lead the proper gas through the sealed-in tube (fig. 15). These flasks may be used advantageously for steam distillations.

If the ordinary round bottom flask is connected with the condenser by a glass tube bent at a proper angle and passing through the stopper of the flask, the tube should be cut off at a sharp angle (fig. 16); it should have a hole slightly above the end to permit the passage of the gases so that the drops adhering to it will not be carried into the distillate, but will fall back into the flask.

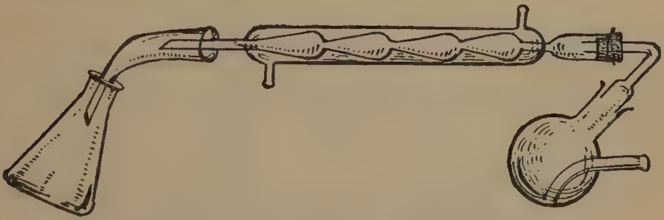

FIG. 15. TUBE-FLASKS (MÜLLER)

In more exact investigations, distillations must be carried out in apparatus higher than retorts or ordinary round flasks, to avoid errors due to mechanical transfer of the material being distilled into the distillate. This is of great importance in the quantitative determination of nitrogen by the Kjeldahl method. The adapters specially constructed for this purpose will be described under the heading "Analysis of Organic Materials." One of the queerest cases of this kind, of the highest scientific interest in earlier days, was cleared up by Berzelius[12] in 1830.

At that time Gmelin still upheld the views of those who believed that lactic acid was very closely related to acetic acid, and could be purified by distillation with water, in that it was transformed into the latter by this operation. Scheele, in 1780, was the first to suggest that sour milk, whose souring had been ascribed, up to that time, to the formation of acetic acid, contained a separate acid, namely lactic. Gmelin believed lactic acid to be acetic acid combined with an animal material, and his chief reason for this assumption was that solutions containing lactic acid, when distilled, gave a distillate which reddened litmus paper slightly, and, if evaporated after the addition of barium hydroxide, the distillate finally left a film which developed the odor of acetic acid, when treated with sulfuric acid. Berzelius repeated the experiment and obtained the same results as Gmelin, only he found that the odor was due to traces of hydrochloric acid and not acetic acid; the hydrochloric acid being present in the lactic acid. To decide the question, he mixed potassium lactate with a slight excess of tartaric acid and carefully distilled the mixture until about nine-tenths had gone over. The distillate, when evaporated, gave some lactic acid, and during the further evaporation to dryness, crystals appeared which left a trace of potassium acid tartrate when dissolved in alcohol.

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[12] Berzelius, J. J., *Pogg. Ann.*, **19**, 26 (1830).

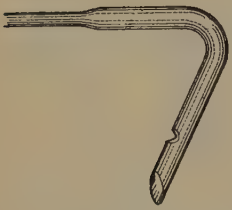


FIG. 16. DISTILLATION TUBE

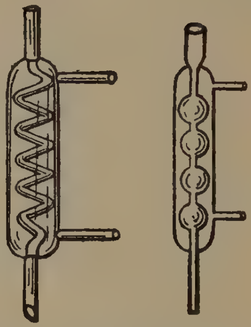
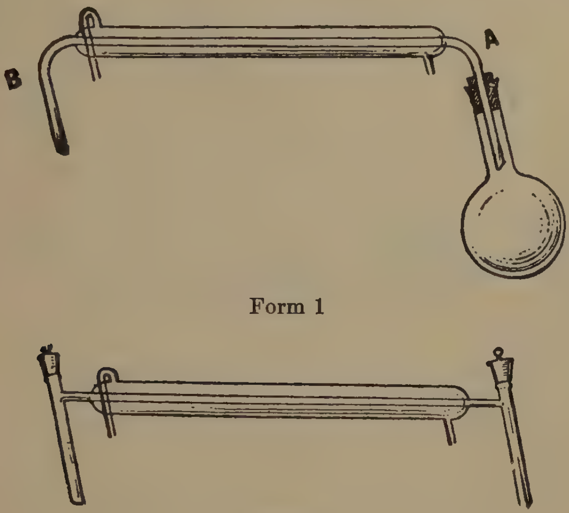


FIG. 17. VARIOUS FORMS OF LIEBIG CONDENSERS

This showed, as Berzelius said, how seldom it is possible, when using such low distillation apparatus as a retort, to prevent a portion of the fine mist formed from the breaking of the bubbles during the boiling, from being carried along with the water vapor into the neck of the retort and thence into the distillate. Only when redistilled, did the distillate lose every trace of acid and of potassium bitartrate, which could not have occurred if it had contained acetic acid, and he thus showed that lactic acid cannot be transformed into acetic acid by distillation.[13]

The inner tube of the Liebig condenser should not be too narrow if it is to be conveniently connected with the retort or with the flask and since the efficiency of the condenser depends on the extent of the cooling surface. To increase the contact between the gases to be cooled and the condenser walls, a narrow tube of the proper size, sealed at both ends, may be placed in the cooling tube. It is supported by protuberances at various places. The cooling tube is somewhat indented at its lower end to prevent the other tube sliding through it. The introduction of such a tube permits the rapid distillation of ether without loss, through even comparatively short condensers, through which ether vapor ordinarily passes largely uncondensed. Successful attempts to diminish the somewhat awkward lengths of straight condensers have been made by enlarging the cool-



Form 1

Form 2

Fig. 18. Montagne Condensers

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[13] The same effect is forcibly exemplified by the distillation of solvent from an alcoholic solution of a dye, it being found impossible to obtain a colorless distillate on one distillation unless an efficient column is employed.—H. T. C.

ing surface of the inner tube and by shaping it into bulbs and coils. These condensers are usually blown from one piece of glass so that all rubber connections are eliminated and leaks avoided[14] (fig. 17).

The frequent attempts to devise condensers more efficient than the Liebig type show that these, even in modified form, do not satisfy all requirements.

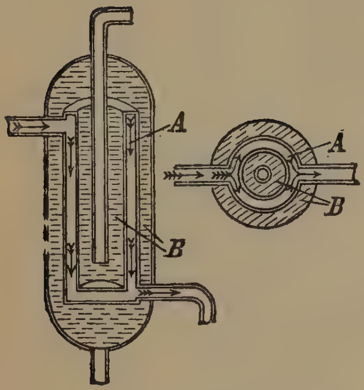

Fig. 19. Metal Condenser (Hanfland)

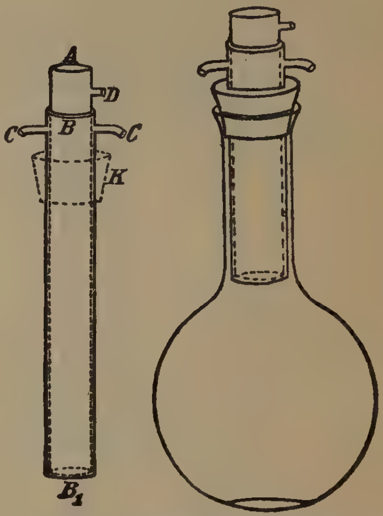

Fig. 20. Walther Condenser and Method of Fastening to Flask

Montagne[15] modified the inner tube of the condenser so that neither the vapors nor the distillate come in contact with cork or rubber, even though, when using Form 2 (fig. 18) it is necessary during the distillation to add materials to either the liquid being distilled or the distillate. These openings may be used for thermometers.

Hanfland[16] has devised the following efficient and handy metal condenser for ether vapors. These must pass through a very narrow space, *A* (2 mm.) between two cylindrical jackets, being cooled on both sides of this space by running water which enters the top of the condenser, fills the inner cylinder, runs from above down over the outer cylinder, and leaves the condenser at the bottom (fig. 19). The condenser is 16 cm. high and 4 cm. in diameter, and may be fastened to a stand. It may be used for the distillation of all materials which are liquid at the temperature of the cooling water.

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[14] The Liebig type of condenser may be rendered more rugged by replacing the usual thin glass jacket by a brass tube into which brass side-arms of suitable size are soldered near each end (preferably on opposite sides of the tube). The inner tube is held in place by bored indiarubber or cork stoppers. Such a condenser may be firmly held in a clamp without danger of breaking. —H. T. C.

[15] Montagne, P., *Ch. Weekbl.*, **10**, 960 (1913).

[16] Hanfland, Fritz, *Ch. Zt.*, **26**, 1109 (1902).

Walther's[17] condenser which has found much favor will now be described. This condenser which combines most efficient cooling with great convenience, was devised for extended studies in which liquids had to be added to a reaction mixture, the evolved gases collected, and yet permit frequent shaking of the boiling flask. It may be easily made from glass or metal. Figure 20 shows the metal form. *A* and BB_1, are two thin metal tubes, differing slightly in diameter, which are sealed at the ends B_1 and *B*. *CC* are side tubes for the entrance and exit of the cooling water. The small tube *D* serves for leading off the reaction gases or the air expanded during the heating of the boiling vessel, if tube *A* is closed by a dropping funnel set upon it. The space between the two tubes *A* and BB_1 is separated in the direction from *B* to B_1 as well as front to back by two metal strips, which extend to within a few mm. of the bottom B_1, so that the cooling water flowing in at *C* is forced downward on one side of the condenser and upward on the other.

The second figure shows how the condenser is used by placing it in the neck of the boiling vessel. A cork is ordinarily not required to fasten the condenser, since it may hang directly into the flask, being suspended on the neck of the flask by the tube *C*. The apparatus has a total length of 19 cm.; the cooling surface is 16 cm. long; the external diameter 2 cm.; the width of the tube *A* is 1.2 cm., and the apparatus weighs only 90 grams. The width is chosen so that the condenser may be fitted into flasks of the sizes most commonly used; a connecting piece of glass tubing may be used with smaller flasks, and a cork stopper for wide necked ones. The cooling surface is considerable, since the action of the outer surface of the tube BB_1, is added to that of the inner surface of the tube *A*. The apparatus is most convenient since no clamps are necessary to hold the flask which leaves it movable; the flask together with the condenser can be turned around easily; the condenser may be readily removed and replaced.

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[17] Walther, Reinh., *Ch. Zt.*, **20**, 462 (1896).

The condenser made of nickeled brass is perfectly satisfactory for work in organic chemical laboratories. It may be made of glass in the same external form and following the same principle, but suitably modified with respect to the circulation of the cooling water.

If water does not suffice as the cooling agent, in spite of increased cooling, it is customary to use a coil as condensing tube so that comparatively great lengths may be surrounded by ice or cooling mixtures (for details see heading "Crystallization") as shown in figure 21. The arrangement for water circulation also shown, suggests that these serpentine coolers, because of their considerable length, sometimes give satisfactory results with water cooling, where the Liebig condenser fails.

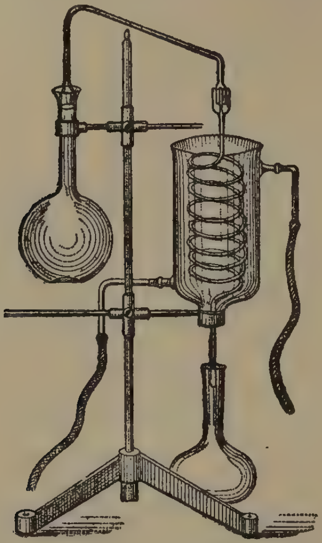

FIG. 21. CONDENSER FOR USE WITH ICE OR FREEZING MIXTURES

The following observations are given apropos of low boiling liquids. According to the earlier data, methyl bromide boils between 13° and 17°. However, in 1905, Steinkopf[18] showed that this value is only obtained if methyl bromide is distilled from an ordinary fractionating flask in which the bulb of the thermometer is a few centimeters above the liquid. If the whole distilling flask is placed in water at 6°, so that the vapor is not heated by the surrounding air, a constant boiling point of 4.5° is observed.

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[18] Steinkopf, Wilhelm, and Frommel, Wilhelm, *Ber.*, **38**, 1868 (1905).

It may also happen that liquids are to be added from time to time, during a simple distillation. Ordinarily, in such cases, a separatory funnel passing through a two holed stopper is used. Rammstedt[19] has devised a special dropping funnel for the particular requirements of quantitative work (fig. 22). He used it, for example, when determining pentosans by Tollens'[20] method, in which several 30 cc. portions of hydrochloric acid are allowed to flow into the distilling flask during the distillation. This also eliminates the two holed stopper.

FRACTIONAL DISTILLATION AND THE THERMOMETER USED

In practically all distillations, it is necessary to know the temperature of the vapor above the boiling liquid, and all boiling point data refer to this unless expressly stated otherwise. Consequently, thermometers should always be placed a few centimeters above the boiling liquid in distillation apparatus.[21]

By a fractional distillation is meant one in which the parts of the distillate are always collected separately; the thermometer varying only a few degrees, if any, while they are passing over. If these fractions are redistilled often enough, products will finally be obtained which pass over while the thermometer varies little, if at all.

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[19] Rammstedt, O., *Z. angew. Ch.*, **26**, 640 (1913).

[20] Kroeber, E., *Journ. f. Landwirtschaft*, **48**, 357 (1900); *Chem. Zentr.*, **72**, I, 477, 1119 (1901).

[21] If the lower end of the thermometer be placed at so short a distance from the surface of the liquid that the vapor has not ample opportunity to attain equilibrium with the liquid which condenses from it (by radiation of heat from the neck of the distilling flask), there is grave danger that the indicated boiling point will be too high, especially if the rate of distillation be rapid. For this reason it is advisable to situate the sidearm of the distilling flask at a point in the neck removed from the bulb by a distance at least equal to the diameter of the latter. On the other hand, the thermometer must carefully be kept as far as possible from the wall of the neck; if it lie close to it, or especially if it come in contact with it, heat may radiate from the thermometer more rapidly than it is supplied by the vapor, resulting in too low a reading. —H. T. C.

With very few exceptions, a chemically pure distillate has then been obtained by fractional distillation.

The most sensitive test as to the homogeneity of a distillate, according to Michael,[22] is to redistil a supposedly pure distillate obtained by fractional distillation, and collect it in three parts, and then determine the density of each.

Thermometers break frequently when pushed directly through cork or rubber stoppers, and this occurs more frequently when removing them after use. To avoid this the writer uses a device somewhat like the stuffing boxes of machines. The glass tube *ab* (fig. 23) goes through the stopper and is wide enough to permit the passage of the thermometer. Over the outer end of this tube is slipped a piece of rubber tubing *c*, of the proper width, and this holds the thermometer after it has been pushed through. After the apparatus has been set up, the thermometer may be easily introduced with the aid of this device, and as easily removed at the end of the operation.

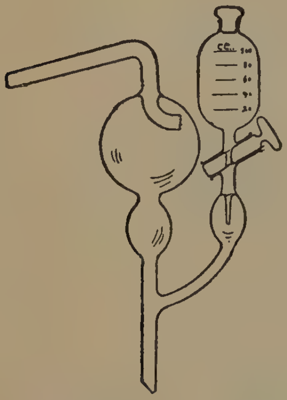

Fig. 22. Dropping Funnel (Rammstedt)

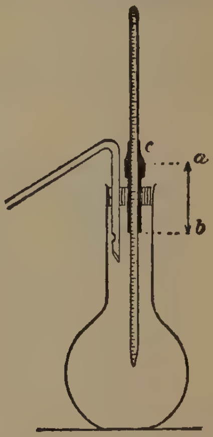

Fig. 23. Method of Fastening Thermometer in Stopper (Lassar-Cohn)

If leaks are found in complicated distillation apparatus, a current of air may be drawn by an air pump through the whole apparatus, making the loss of the vapors impossible.

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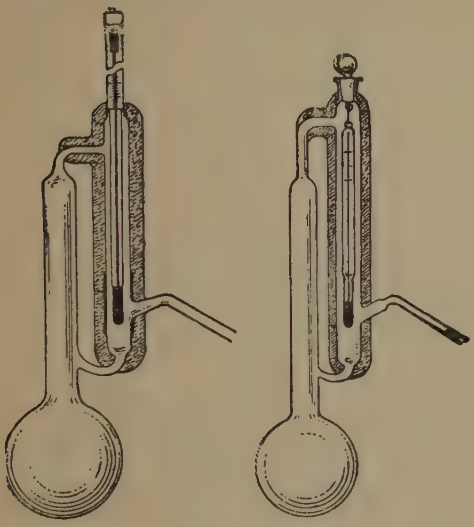
[22] Michael, cited by Brunel, R. F., *Ber.*, **44**, 1003 (1911).

If at all feasible, the boiling point of the distilling liquid is taken with the stem of the thermometer immersed in the vapor of the boiling liquid up to the indicated temperature. This is accomplished by using small flasks on which the side tube is sealed at a sufficient height. The flasks ordinarily used only permit this in a few cases; usually part of the thermometer extends out of the vapor and it is then necessary to make a correction for this part.



Form 1 Form 2

FIG. 24. FLASKS FOR EXACT BOILING-POINT DETERMINATIONS (RICHARDS)

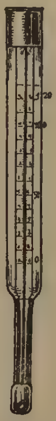


FIG. 25. HAHN'S THERMOMETER WITH SILVER-PLATED VACUUM JACKET. (DEWAR FLASK)

Baeyer[23] made the excellent suggestion that this correction be determined by distilling, in the same apparatus, another liquid of a similar, but accurately known, boiling point. In this way, both the errors of the thermometer and the influence of barometric pressure are eliminated. It would be desirable if collections of such liquids could be purchased in the same way as scales of hardness, for instance.[24]

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[23] Baeyer, Adolf, *Ber.*, **26**, 233 (1893).

[24] At the present time thermometers are available which are calibrated for "3-inch immersion." The readings on these are correct when the thermometer extends 3 inches into the vapor and the stem is at room temperature.—E. E. R.

According to Kopp[25] the necessary correction may be made as follows: a thermometer is placed, by means of a cork, in the tubulure of the retort in which the liquid is to be heated, and the position of the thermometer scale is noted during the distillation. A second thermometer, whose position may be changed, is placed with its bulb close to the tube of the inserted thermometer at the middle of the mercury column which extends above the cork during the determination of the boiling point.[26] It is desirable to diminish the effect of the flame upon the air surrounding the exposed mercury column by a horizontal shield placed just above the cork. The corrected boiling point is then equal to $T + N\ (T - t) \cdot 0.000154$, in which T is the observed boiling point, t the temperature of the auxiliary thermometer and N the length of the exposed mercury column from the middle of the cork to T.

The forms of distillation apparatus recommended by Richards[27] are well suited for exact determination of the boiling point in fractional distillations. Both forms are clear from figure 24. Form 1 is provided with a Beckmann thermometer, Form 2 with a small Anschütz thermometer (see below under "Thermometers"). Both have glass stoppers and a quartz window for reading the thermometer in the asbestos covering surrounding the side tube. The long path that the vapor must traverse to reach the condenser is an advantage as neither spray nor superheated vapors can reach the thermometer. The essential feature is that the whole length of the thermometer is exposed to the temperature of the vapor and the bulb is just at the exit to the condenser, consequently the temperature shown is that of the vapor just about to condense. For greater accuracy the whole apparatus may be insulated with asbestos and panes of mica are inserted on the proper side so that the temperature may be read. The whole apparatus is then placed in an asbestos jacket or an air bath.

The boiling point of any liquid is dependent on the atmospheric pressure to which it is subjected. According to Landolt,[28] in the neighborhood of the normal barometric pressure the boiling point diminishes 0.0430° for each millimeter decrease in pressure. At present it is customary, though incorrect, to state the air pressure at which the boiling point is determined, instead of recalculating the latter to normal pressure.

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[25] Kopp, H., *Ann.*, **94**, 263 (1855).

[26] Since an error of less than 5° on the temperature of the stem does not materially alter the correction, the temperature of the stem may be estimated sufficiently closely by the finger.—E. E. R.

[27] Richards, T. W., and Barry, F., *J. A. C. S.*, **36**, 1787 (1914).

[28] Landolt, H., *Ann. Supl.*, **6**, 175 (1868).

Staedel and Hahn[29] constructed an apparatus in which it is possible to carry out distillations and boiling point determinations at varying desired air pressures. Such determinations are rare, excepting distillations at very low pressures, which are to be discussed later, and their apparatus will only be mentioned here. The criticisms[30] of it were not justified; but Schumann[31] later proposed some improvements.

THERMOMETERS

The following statements about the thermometer may be of interest. It is not correct to call the thermometer scale used in scientific work the Celsius scale, since on this, the freezing point of water was taken as 100° and the boiling point as zero. The inversion of these numbers was made by Linné about 1740. Zincke[32] was the first to point out the convenience of thermometers whose graduations began at 100° just over the bulb, for high boiling liquids, so that without making the thermometer too long, the single degrees did not lie too close together.

Later Graebe[33] proposed the use of short thermometers whose mercury columns are entirely surrounded by vapor or else extend out of it, only a little, making their errors very small. Correct boiling points may be obtained with any thermometer if it is compared with four exactly calibrated ones, the first extending as high as 100°, the second with the lowest reading at 100°, the lowest reading of the third being 216 to 218°, (boiling point of naphthalene) and that of the last being 304 to 306°, (boiling point of benzophenone). The comparison must be made, of course, under closely similar conditions.

Anschütz[34] attained greater accuracy by dividing the thermometer scale among seven short thermometers whose degrees were further divided into fifths, and so kept the mercury column from projecting beyond the vapor of the boiling liquids. Sets of such thermometers are sold by larger apparatus dealers.

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[29] Staedel, W., and Hahn, E., *Ann.*, **195**, 218 (1879).

[30] Staedel, W., *Ber.*, **13**, 839 (1880).

[31] Schumann, O., *Wied. Ann.*, **12**, 44 (1881).

[32] Zincke, Th., *Ann.*, **161**, 95 (1872).

[33] Graebe, C., *Ann.*, **238**, 320 (1887).

[34] Anschütz, R., *Destillation unter vermindertem Druck*, Bonn, 1895, p. 30.

In general the following is true: If a normal thermometer is thrust into the vapors of a liquid which boils, say, at 200°, immersing only the bulb one time, and the entire length the second time, there will be a difference of 5 to 6° in the readings.

The thermometers devised by Hahn[35] in 1914 best eliminate the unpleasant circumstances attendant upon temperature determinations. In these, the capillary is surrounded by a vacuum jacket (fig. 25). This second glass jacket surrounding the capillary as well as the scale, is completely evacuated and its lower end is covered with a silver mirror for 10 to 15 cm. If this acts as a Dewar flask and the radiant heat cannot reach the thread to this height, 15 cm. will suffice for most laboratory cases. The calibration of the commercial thermometer is carried out in such a way that it is only exposed to the calibrating temperature over the part protected by the silver mirror.

Sometimes when thermometers, and especially those having a scale on the stem, have been in use, surface flaws and cracks develop, apparently spontaneously. According to Kühn,[36] in most cases they may be ascribed to improper use and the sensitiveness of Jena thermometer glass. A thermometer should, if possible, be heated along with the substance. Otherwise it is best, in measuring high temperatures, to rapidly dip it in and take it out several times. After using a thermometer at high temperatures it is essential to hang it up until it has completely cooled, avoiding contact with any material whatsoever as well as drafts. Normal thermometers treated in this way only break if they are wiped off too soon with waste or cloths after being removed from oil or saltpetre baths. Thermometers must be stored so they are not pressed against, or scratched by hard objects. Even knocking glass against them may cause them to break.

The non-varying composition of the different Jena thermometer glasses whose expansion, melting point, depression, etc., have been investigated by the Physikalisch-Technisch Reichsanstalt, Charlottenburg, has made this glass very desirable for the manufacture of thermometers. In only one respect is it more sensitive than ordinary glass. Therefore, in practice, as well as in the whole glass industry, excepting for quartz glass, which no temperature change affects, the rule is, "Heat slowly and cool even more slowly." In this way are avoided the apparently spontaneous hair cracks and fractures really due to tension caused by too rapid heating or cooling.

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[35] Hahn, H., *Zeit. f. angew. Chem.*, **27**, 241 (1914); see also Dimmer, G., *Zeit. f. angew. Chem.*, **28**, 255 (1915).

[36] Kühn, A., *Ch. Zt.*, **32**, 985 (1908).

The successful attempts made since 1890 to use mercury thermometers in the ordinary way, even above the boiling point of mercury, that is above 360°, will now be discussed.

Thermometers of ordinary construction in which there is a vacuum in the capillary above the mercury may be used, according to Mahlke,[37] only up to about 300°, because, if heated higher, the mercury begins to boil. If, however, the mercury in the capillary is under pressure, the boiling does not begin except at higher temperatures, and the working range of these instruments may be extended in this way. Therefore, since 1890, at the suggestion of the Physikalisch-Technischen Reichsanstalt, thermometers have been made which are reliable up to the softening temperature, 450°, of this variety of glass. They are made by filling the space in the capillary above the mercury with nitrogen at atmospheric pressure, and the volume of this space is so proportioned that when the thermometer is heated, the rising mercury compresses the nitrogen above it, and the pressure produced is sufficient to prevent boiling at 450°.

When constructing instruments for still higher temperatures, the nitrogen must be introduced at pressures greater than that of the atmosphere. In this way, thermometers[38] made from a variety of glass discovered later, may be used up to 550°. In these, the mercury attains a tension of more than 17 atmospheres so that it is necessary to fill the space in the capillary above the mercury with an indifferent gas at a pressure of almost 20 atmospheres, to prevent the boiling of the mercury. This is most easily accomplished with liquid carbon dioxide.

When using these thermometers at the highest temperatures for which they are reliable the same difficulty mentioned before, is encountered. In order to make a reading it is necessary that part of the mercury column extend out of the temperature bath. The thread will then not be at the same temperature as the thermometer bulb and this makes necessary a correction of the reading, which at the temperatures under consideration may amount to as much as 40°.

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[37] Mahlke, A., *Ber.*, **26**, 1815 (1893).

[38] Schott, O., *Zeit. f. Instrumentenkunde*, **11**, 330 (1891); see also Baly, E. C. C., and Chorley, J. C., *Ber.*, **27**, 470 (1894); see also Wiebe, H. T., *Zeit. f. Instrumentenkunde*, **10**, 207 (1890).

The conditions attending the exposed column are extremely variable so that the older formulae set up for this correction do not give universally valid results, and if applied, errors amounting to one half the total correction may still be present. Even if the estimation of these is attempted by placing an auxiliary thermometer at the middle of the exposed part of the mercury column, considerable errors will still remain, since first, the second thermometer will only, in exceptional cases, indicate the average temperature of the first, and secondly, only seldom is it possible to determine exactly the point at which the temperature of the column begin to differ from that of the bulb.

Both sources of error may be avoided by using an accessory instrument devised by Mahlke,[39] which makes possible the direct reading of the desired correction. It consists of a thermometer made up of two capillaries, one wide and one narrow. The wide one forms the bulb of the thermometer so that it differs from an ordinary thermometer, in that the reservoir is drawn out to a thread. The scale is applied to the narrower capillary, next to which an auxiliary scale may be placed for directly reading the desired correction.

The instrument which he calls a "thread thermometer" is used as follows. It is placed next to the real thermometer so that the contracted part where the wide capillary joins the narrow one is somewhat below the head on the thread of the thermometer. The reservoir of the thread thermometer must be long enough so that its lower end will still extend into the temperature bath. If, under these circumstances, the thermometer indicates the temperature T^1, the thread thermometer t^1, the desired correction will be $(T^1 - t^1)\dfrac{r}{L}$ where r is the length from the bulb of the auxiliary instrument expressed in thermometer degrees, and $L = n + T^1 - r$, if $\dfrac{1}{n}\left(= \dfrac{1}{6080}\right)$ is the relative coefficient of expansion of mercury in Jena glass 59.$^{\text{III}}$

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[39] Mahlke, A., *Zeit. f. Instrumentenkunde*, **12**, 58 (1893).

The quantity $\frac{r}{L}$ is almost constant over wide temperature ranges so that the desired correction is nearly proportional to the difference $(T^1 - t^1)$. If then, the value $\frac{r}{L}$ is placed next to the scale of the thread thermometer, and expressed in the latter's degrees, starting at zero, and indicating the divisions by 0, 1, 2 . . . ., then the correction may be read directly. It is only necessary to determine the difference $(T^1 - t^1)$ of the readings of the two instruments on the temperature scale and the desired figure will be given by the adjacent value on the auxiliary scale. The determination of the correction for the exposed portion is very easy when this auxiliary instrument is used.

The glass thermometers suitable for high temperatures are being gradually replaced by quartz ones. Pure quartz may be fused to a mobile liquid in electric furnaces in iridium vessels so that it becomes soft enough for experts to work it in small quantities, as they do ordinary molten glass. Siebert[40] states that only mercury (but not potassium, sodium or tin) is suitable for filling thermometers of fused quartz. If they contain nitrogen under 20 atmospheres pressure they may be used up to 580°, and a pressure of 60 atmospheres raises this to 720°, and so on.

Kühn[41] states that quartz glass thermometers are now available in all the forms, either flat or round, and for all temperature intervals up to 750°. Quartz glass, because of its low coefficient of expansion, remains unaffected by all temperature changes, and consequently shows no thermal after-effects. In addition, the disadvantages shown by all other glasses, such as breaking due to sudden great temperature changes, cracking through condenser water dropping upon them, and fractures resulting from strains, present in all kinds of glass, loss of usefulness through overheating, rise of the ice point because of thermal after-effects, etc., are completely eliminated. A permanent constant temperature reading is thus insured. Quartz glass thermometers, unless broken by carelessness, have an unlimited period of usefulness and have the great advantage that they will indicate temperatures about 200° higher than will other glass thermometers. They are checked up to 700°C. by means of certified resistance thermometers and their accuracy is satisfactory. Up to 750°, quartz glass thermometers suffer no injury through overheating, because the softening point of the quartz is still about 500° higher than the highest division of the scale.

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[40] Siebert, C., *Z. Elektroch.*, **10**, 158 (1904).

[41] Kühn, A., *Ch. Zt.*, **34**, 339 (1910).

Electric thermometers are also very convenient for determining higher temperatures. They are of particular interest when working with explosive materials since the scale may be set up at any desired distance.

FRACTIONAL DISTILLATION WITH STILL HEADS

Fractional distillation,[42] that is, the separation of mixtures of liquids volatile without decomposition, utilizing the differing boiling points of the chemical individuals present, may be aided by certain devices copied from the distilling columns used in technical practice. Often the separation can only be accomplished in this way.[43]

At the suggestion of V. Meyer, Kreis[44] in 1884, tested the efficiency of the best of such apparatus known up to that time. The gauze still head suggested by Linnemann and the Hempel columns proved best for the fractional distillation of substances boiling around 100° (fig. 26). The Hempel device consists of a tube filled with glass beads or porcelain marbles and is better than the Linnemann apparatus because it is easily made and is all of glass. By this method, one distillation gave the same results as twelve distillations from a flask without a still head.

Meanwhile the Raschig[45] rings proved most efficient in the technical column stills. It seemed then only logical, in the laboratories, to substitute glass tubes piled on each other without order, for the glass beads. But they did not prove efficient. As a basis for another patent[46] its author[47] showed that a glass tube filled with tubular thin walled glass beads is not as good as one filled with polished beads. In fact, in attempting a sharp separation of different liquids, tubular glass beads are the least suitable filling.

[42] This may also be called interrupted distillation.

[43] Hill, H. B., *Ber.*, **22**, 607 (1889).

[44] Kreis, H., *Ann.*, **224**, 259 (1884).

[45] Raschig, F., German patent 286122 (1914); *Chem. Abstr.*, **10**, 958 (1916).

[46] Sudenberger Maschinenfabrik u. Eisengiesserei, German patent 310966 (1918); *Chem. Zentr.*, **90**, II, 805 (1919); see also Rüdiger, *Chem. Zt.*, **43**, 411 (1919).

[47] Herr, V. F., *Ch. Zt.*, **32**, 148 (1908).

For small quantities of material or for substances which attack cork, rubber, etc., Hantzsch[48] recommended, that, instead of placing a separate still head containing beads on the fractionating flask, the beads be placed directly in the elongated and widened neck of a flask. The beads are held in place by platinum or nickel gauze placed over the bulb of the flask. The view has often been expressed that flasks with lengthened globular necks are preferable to those with removable superimposed bulbs (fig. 27).

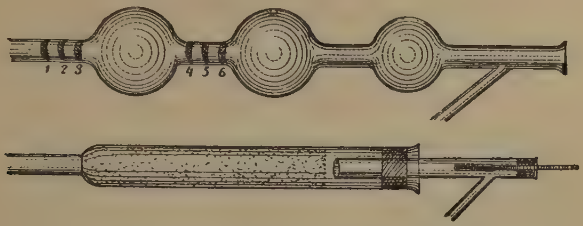

Fig. 26. (*Upper*) Distillation Tubes (Linemann)
(*1, 2, 3, 4, 5, 6* are small baskets of platinum wire)
(*Lower*) The Packing Consists of Glass Beads (Hempel)

The numerous column still heads, some of which have been used for more than forty years, have not satisfied all requirements.[49] It has been found that a sharper fractionation is possible only if the columns are not exposed to the air, but are kept at definite temperatures. Several types of apparatus constructed on this principle will

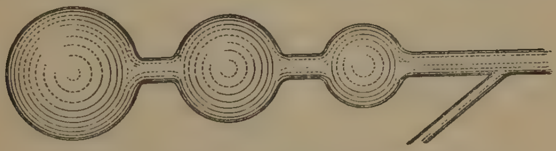

Fig. 27. Flasks with Bulb-Extension

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[48] Hantzsch, A., *Ann.*, **249**, 57 (1888).

[49] The principal deficiency of almost all laboratory distilling columns lies in their failure to provide adequate interchange between ascending vapor and descending condensate (cf. *Ind. Eng. Chem.*, **18**, 1092 (1926)). An excellent discussion of the merits of various types of column is to be found in an article by J. B. Hill (this will probably appear shortly in *Ind. Eng. Chem.*).—H. T. C.

be discussed. The problem at hand determines the choice, and even the extreme demands of Ekenberg may be satisfied.

The still head (fig. 28) of O. Baum[50] has an advantage over the older types, since in it, the distillation proceeds as it does in the fractionating columns provided with capsules, so generally used in technical practice. It is, therefore, an adaptation of this still head to laboratory practice and accomplishes a rather perfect fractionation. The dephlegmator above is filled with paraffin oil, and during the distillation its temperature is constantly kept 10° below the temperature of the distilling liquid. This is accomplished by properly regulating, by means of a pinch clamp, the flow of water into the small cooler of the dephlegmator which is connected by means of a T tube with the water pipes. (If the boiling temperature is much above 100° the cooling is diminished correspondingly by raising the small cooler.) The condensate flowing from the dephlegmator collects in the individual bulbs. The vapors coming from below pass through the ∩ shaped tubes (which correspond to the capsules of the capsule column). The vapors are thus forced to bubble regularly through the condensate, accomplishing a complete dephlegmation. Since the dephlegmator delivers the necessary condensate, the apparatus must be protected against cooling and consequent unnecessary condensation by an asbestos cover. The apparatus works quietly and regularly (without any choking), this being the reason for its more efficient action as compared with the earlier types. It accomplishes in one distillation an almost complete separation of the components of a mixture, only very small quantities of middle fractions being obtained. The apparatus has been found of especial value for completely fractionating very low boiling substances, such as ethyl chloride, whose separation is often difficult, despite great differences in boiling points (see the discussion of ethyl bromide above). In this case, the dephlegmator should be cooled directly with water and without the intervention of the paraffin oil. The apparatus gives very good results at medium temperatures (100 to 200°) even if it is used without the dephlegmator. Under such circumstances, it is used like the ordinary apparatus without asbestos jackets, being cooled by the air. On the other hand, the use of the paraffin dephlegmator is particularly recommended for temperatures ranging from 200° upward. There are two forms of the apparatus, one having four and the other five bulbs. The smaller form is for quantities up to about 50 grams while the larger one will completely fractionate several kilograms of liquid at a satisfactory rate.

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[50] Baum, E., *Ch. Zt.*, **35**, 497 (1911).

The Hempel boiling tubes[51] serve for simpler cases, and in them the dephlegmator of the Baum apparatus is combined in a simple way with the rectification striven for by Linnemann. The vapors to be separated pass through the part of the tube *A* (fig. 29) which is filled with beads, and they are partially condensed by the liquid flowing through *B*, and are rectified by the vapors coming in the opposite

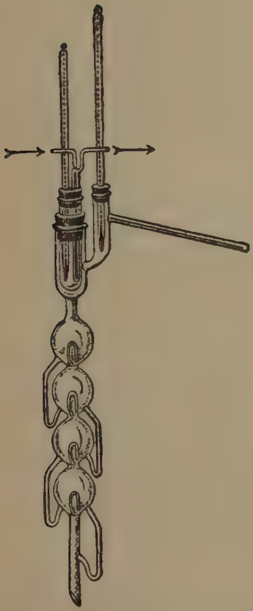

FIG. 28. FRACTIONATING TUBE (BAUM)

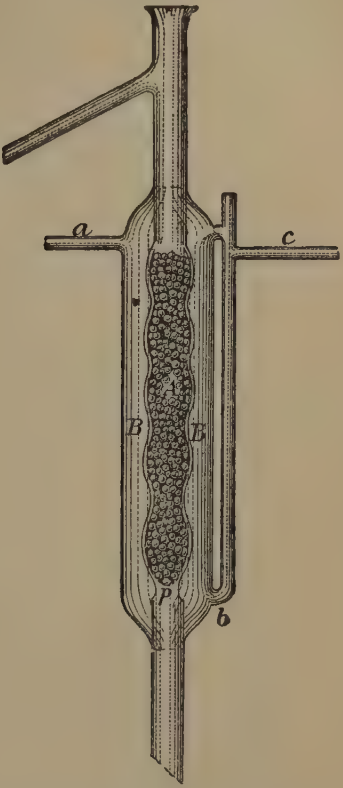

FIG. 29. HEMPEL'S NEW DISTILLATION TUBE

[51] Hempel, Rud., *Ch. Zt.*, **10,** 371 (1886).

direction, while flowing back over the beads. The dephlegmating liquid enters *B* through *a*, passing *b*, leaving through *c*. The flow in this direction causes the layers of liquid in the lower part of *B* to be warmer than those above. In this way, a considerably better separation of the less volatile constituents of the vapor is attained, since the rectifying action of the stream of vapor is further aided in that the liquid flowing down over the surfaces of *A* pass from cooler to warmer areas. According to Hempel, this tube is particularly suitable for the separation of liquid mixtures boiling below 100°, since, in this case, the water flowing from the condenser may be used as a dephlegmating liquid. The upper exit of the condenser is simply connected with *a*, by a rubber tube. The dephlegmating water is easily brought to the proper temperature by increasing or decreasing its rate of flow into the condenser. The device may be used for all other mixtures of liquids if a suitable dephlegmating liquid (amyl alcohol, glycerine, etc.) is provided.

The proper choice of beads is essential to the efficient working of the apparatus. For mobile liquids, beads of 4 to 5 mm. diameter should be used, while for high boiling and viscous ones, the beads should be 6 to 7 mm. or more. The platinum gauze *P* should be wide meshed.

Kahlbaum,[52] in 1896, showed in detail the necessity of a double vapor jacket for every boiling point determination making any claims to accuracy. He uses the vapor of the boiling liquid itself as this jacket. The novelty of his "Normal Boiling Tube" is that the thermometer bulb is not surrounded by a tube introducing the vapors, but by the one carrying them to the condenser (fig. 30). This arrangement makes it impossible, even with vigorous boiling, for particles of the boiling liquid ever to reach the thermometer which is surrounded with vapor over its entire length. The principle of a double vapor jacket is maintained, and since the inner tube is free at one end there is no danger of strains in the glass causing breakage, with its unpleasant consequences. It is a further advantage that the liquid, after coming in contact with cork, flows back into the flask along the outer walls and does not get into the receiver.

The fractionation of some liquids, as, for example, Caucasian petroleum, presents special difficulties. How such difficult cases may be solved is shown by the following example.

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[52] Kahlbaum, Georg W. A., *Ber.*, 29, 71 (1896).

In order to fractionate a mixture boiling over wide ranges, as naphtha does, it is necessary to use shorter still heads as the boiling points rise, but this decreases the sharpness of the separation. For this reason, the devices proposed by Herr[53] failed almost completely at temperatures exceeding 180 to 200°. Accordingly, he attempted to assemble from ordinary laboratory utensils apparatus which would be accurate, keeping in mind the boiling points of the liquids to be distilled. For years he obtained excellent results with the still head described here. His still head (column) was made from a jacket of a Liebig condenser 30 to 100 cm. long. The inner tube was

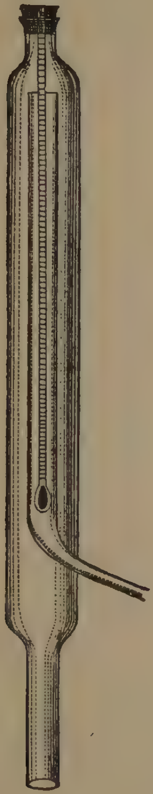
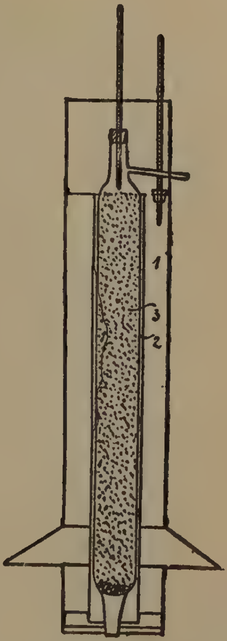


FIG. 30. KAHLBAUM'S DISTILLATION TUBE



1, Air jacket to be heated
2, insulating air space
3, shot-filled column

FIG. 31. DEPHLEGMATOR (HERR)

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[53] Herr, V. F., *Ch. Zt.*, **32**, 148 (1908).

removed, the lower water exit sealed off, and the connection with the condenser was made to the upper water exit by an adapter (fig. 31). A small netting was placed in the jacket to hold the lead shot filling in place. The size of the shot was so chosen that there were about 6 to the gram. The thermometer is introduced above. It is best to support the column by a ring wound with asbestos because its great weight may crush the boiling flask. As boiling vessels, it is advisable to use round flasks with the shortest possible necks; all of the flask should be buried in the sand bath, and there should be no exposed uninsulated glass parts. Five liters may be worked up at one time. After the distillation starts, the temperature rises almost automatically, and three or four units may be supervised at the same time. The columns are insulated with cotton wool, filter paper, and asbestos. If the 100 cm. column is to be used for fractionations higher than 130°, only a thin asbestos insulation is used and the heating jacket, whose construction is evident from the figure, is employed. This jacket is made of riveted, strong sheet copper. The essential characteristic of this jacket is that there is an air space between the jacket heated to 300° (control thermometer) and the column, and this space is progressively heated as the temperature of the column gradually rises. On the one hand, this avoids superheating of the vapors being drawn off, and on the other, the jacket cannot harmfully act as "condenser," with rising temperature of the contents of the column. Aided by this jacket, heated with four burners, the column will fractionate liquids up to 330°. When starting the column, the liquid should be brought to a boil very gradually, or the column will not have time enough to warm up, and will then be filled with condensate and the dephlegmation will cease. In fractionating above 100°, it is best to heat the column and the jacket in advance. If, at any time, the column should fill with liquid, the work must be interrupted and the column dried by a current of air. The method of recovering naphthene is as follows: naphtha is first separated, as is customary in technical practice, into distillates according to their specific gravities, by means of superheated steam and bottom firing. These distillates are then separated into ten-degree fractions from 5-liter round bottom flasks carrying suitable still heads. These are then refractionated with 30 to 40 cm. columns, and finally, constant boiling fractions are obtained with the aid of 80 to 100 cm. columns. The boiling points are considered constant when not less than 95 per cent of the fraction passes over at the same temperature, which usually requires 4 to 5 fractionations. It is possible to fractionate liquids boiling around 0° by lengthening the column and by using suitable freezing mixtures. This was necessary in the search for trimethylene and its homologues supposedly present in the naphtha.

The light oil derived from naphtha tar was fractionated with the aid of this column, and a sharp separation of benzene and its homologues was accomplished.

In 1892, Eckenberg[54] showed that there was no apparatus available suited to the fractional distillation of liquids with a boiling point higher than water, say, 100 to 250°. Of course, it was not impossible to enclose a le Bel tube, for example, in an air bath heated to the desired temperature, but this complicated the apparatus greatly and it was very difficult to regulate the temperature satisfactorily and to keep it constant. Consequently, it is customary, when distilling liquids with high boiling points, to do as he did and use a simple flask with a lateral exit tube. Any one who has worked with such flasks knows that it is very difficult to obtain consistent results in running control distillations, even though the same flask and the same quantity of liquid are used. The reason is, that the vapors do not have to traverse a sufficiently long path to be separated. His experiments showed that the neck of the flask must be at least 25 cm. long. The distillation is then very slow, particularly of the fractions of higher boiling points, and nevertheless a considerable quantity of liquid particles are carried over.

If the long neck of the flask is replaced by a slanting tube about 4 to 5 mm. in diameter and 90 cm. long, these dimensions being determined empirically—by boiling liquids to which non-volatile dyes have been added—and if this tube is heated in an air bath at a definite temperature, it will be found that no liquid particles are carried over. The tube is inclined in such a way that everything condensing at the fixed temperature will run back. If the temperature in the air bath is constant, the long tube will completely separate the vapors. The construction of Eckenberg's apparatus is apparent from the illustration (fig. 32). The tube is spiral shaped and at its highest point the thermometer is ground into it. The glass spiral is enclosed in an air bath whose upper part consists of sheets of mica so that the distillation may be observed and controlled. The temperature is regulated by an electric thermo-regulator connected with a Stahl contact thermometer. The temperature may also be regulated by partly closing the glass chimney. There is no opening in the top of the apparatus. The ascending warm vapors must pass the lower edge of the glass cylinder before escaping. This makes it possible to regulate the temperature in the heat reservoir within 0.2°. There is a maximum difference of 0.5° between the upper and the lower part of the air bath. As long as the distillation continues it is necessary that the boiling in the flask be fast enough so that some of the higher fractions condense on the inside, and flow back in a uniform stream.

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[54] Ekenberg, M., *Ch. Zt.*, **16**, 958 (1892).

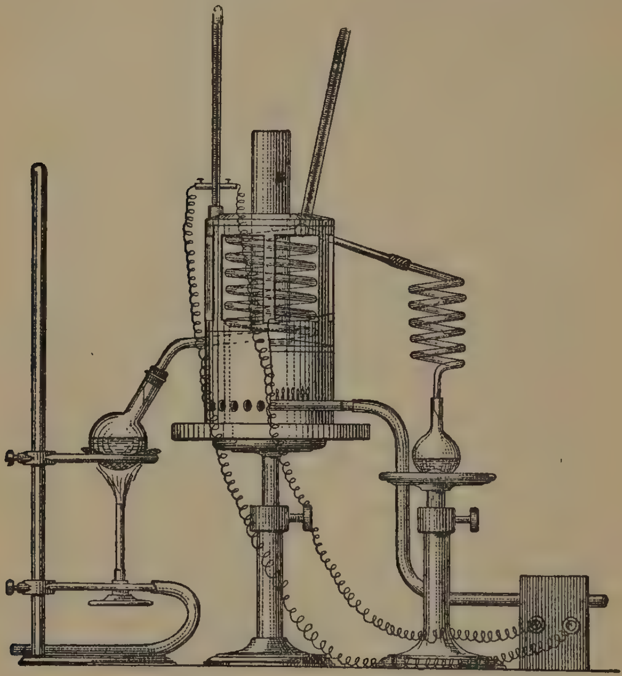

FIG. 32. BOILING-POINT DETERMINATION (EKENBERG)

The example in table 1 is given to show the results obtainable with the apparatus: 150 grams of oil of turpentine were fractionated in a slow stream of carbon dioxide to avoid oxidation and there was obtained by the distillation A and during the check distillation B:

TABLE 1

Results obtainable with Eckenberg's apparatus

	FRACTIONS			
	A		B	
	Grams	Per cent	Grams	Per cent
Up to 130°	3.19	2.13	3.13	2.09
Up to 156.5°	0	0	0	0
At 156.5° to 157°	132.42	88.28	131.90	87.94
Up to 168°	0	0	0	0
At 168° to 168.5°	2.25	1.50	3.07	2.04

Golodetz[55] has devised a most valuable process for separating mixtures of liquids boiling close to each other, or boiling without separation, but it is too extensive to be reproduced here.

REFLUX CONDENSERS

If materials, either wholly or partly volatile are to be heated for some time, they are boiled in a flask or a retort connected with a condenser in such a way that the vaporized portion will be condensed and returned. The pressure in the apparatus may be raised by closing the condenser with a glass tube bent downward, which dips into mercury to a certain depth. If it is necessary to determine whether gases are escaping from the reflux condenser during the heating, it is connected with a Liebig bulb filled with a suitable liquid.[56]

On the other hand, it is often desirable during refluxing to remove the water formed, despite the presence of the condenser. Ephraim[57] accomplishes this by placing a lead tube, through which steam is passed, around the ascending tube. Gabriel[58] bent downward the end of an air condenser arranged in this way; the quantity of the water dropping off indicated how far the reaction had gone.[59] Bischoff[60] used a similar method for immediately removing from the reaction mixture, an easily volatile alcohol split off from a high boiling ester, saponified under a reflux condenser. Sometimes the upright reflux condenser is connected with a second one pointed downward, and the first is kept full of boiling water. A patent[61] recommends that a current of gas be led through the boiling reaction mixture which constantly carries away with it the water formed, without danger of its dropping back.

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[55] Golodetz, A., *Ch. Zt.*, **36**, 273 (1912).

[56] If the upper end of a reflux condenser be not provided with a calcium chloride or soda-lime tube, a surprising amount of atmospheric moisture may be condensed in it and thus find its way into the reaction mixture. Such a guard tube should be employed whenever there is even the slightest objection to the presence of water.—H. T. C.

[57] Ephraim, Julius, *Ber.*, **24**, 1027 (1891).

[58] Gabriel, S., *Ber.*, **18**, 3470 (1885).

According to Volhard,[62] it is advisable to use potash glass retorts if they are to be heated for long periods at high temperatures under reflux condensers, and to cover their bulbs, as was customary before the introduction of gas furnaces, with a thin layer of loam and sand. These coated retorts were used for weeks by him, while uncovered glass which was sometimes ordinary soda glass, seldom lasted for more than one such operation.

Otto[63] makes these coatings as follows: loam or lean clay is ground with water to which a little soda has been added and the thin paste is put on the glass with a brush or feather. When this coat has dried, a second one is put on; this is usually sufficient, although the coating is no thicker than a card. If the whole retort is coated, two small areas opposite each other should be left clear so what is going on inside may be observed.

Winkler[64] recommends three parts of finely ground chamotte and one part of raw clay mixed with commercial water glass solution; this slip is then applied to the glass to be protected. After drying on the sand bath, two or three more coats are put on.

The following protective coating[65] is also recommended. A layer consisting of water glass and cork dust is put on first, and then followed by a second coat of pulverized asbestos and water glass which forms a fire proof layer.

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[59] The same effect may readily be accomplished by the use of a suitable fractionating column in place of the reflux condenser.—H. T. C.

[60] Bischoff, C. A., and Hjelt, Evd., *Ber.*, **21**, 2093 (1888).

[61] Soc. Anonyme Matières Colorantes et Prod. Chim. de St. Denis, German patent 61815 (1891); Fr. III, 101.

[62] Volhard, J., *Ann.*, **253**, 207 (1889).

[63] Otto, F. J., Graham-Otto, *Lehrbuch der Chemie*, 4th ed. p. 127 and 385, Braunschweig, 1863–78.

[64] Winkler, Clemens, *Ber.*, **24**, 1971 (1891); see also Schaal, E., *Chem. News*, **50**, 58 (1884).

[65] Gebr. Stoevesand, German patent 119786 (1899); *Chem. Ztg.*, **25**, 353 (1901).

Figure 33 shows the usual method of mounting a reflux condenser, in case solid substances are to be added, or liquids dropped in during the boiling. If rubber or cork connections are harmful, a long necked flask is used provided with a sealed-on side tube which is sufficiently wide and long to be pushed directly into the condenser tube. If the flask cannot be closed by either rubber or cork, as frequently happens in brominations, for example, a glass stopper must be ground into the opening, or the condenser may be directly ground to fit into an ordinary boiling flask (fig. 34). However, in such cases, the neck should be as long as possible, since ground surfaces are very prone to break when heated, and only in this way can their too rapid heating be avoided.

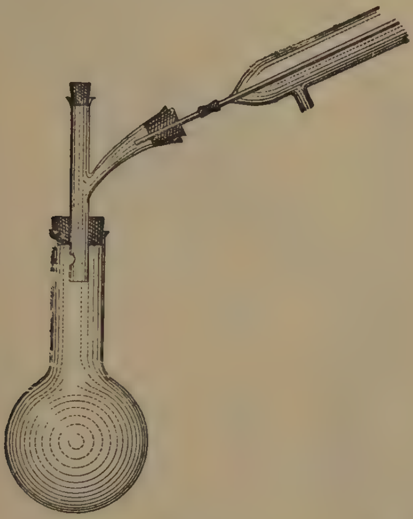

FIG. 33. FLASK WITH ADAPTER FOR REFLUX CONDENSER AND FOR INTRODUCTION OF SOLID SUBSTANCES DURING BOILING

Later, Ascher[66] recommended the condensing arrangement shown in figure 35. In this, the cork connection is eliminated by sealing the condenser directly to a tube of proper width, and the angle of the

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[66] Ascher, R., *Z. angew. Ch.*, **26**, 408 (1913).

T shaped extension should be 60°. In the position shown in the illustration, the condenser serves as a reflux; but, if later the end of the T-tube marked *A* is pushed through the cork, the same condenser may be used for distillation, since it now slants downward. This avoids the tedious and sloppy introduction of materials through the condenser, and also eliminates the use of a stopper between the condenser and the adapter.

Operations in which caustic liquids are to be heated for long periods, and in which all contact with corrodable materials must be avoided, may be carried out in upright retorts with long necks, around which a cooling tube is placed as shown in figure 36. These also permit the gradual addition of solids; liquids may be slowly run in from a dropping funnel, etc. The retort is reversed later for distillation. Of course this may be provided with a tubulure with a glass stopper to facilitate the subsequent removal of the contents.

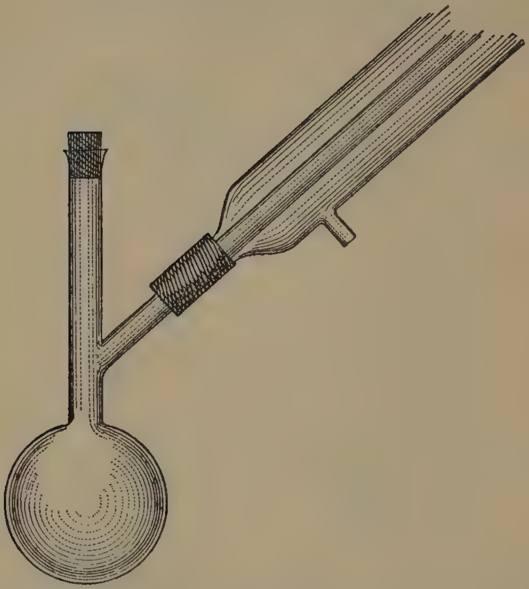

FIG. 34. FLASK WITH GLASS STOPPER AND DIRECTLY CONNECTED REFLUX CONDENSER

The Walther condenser described above is also well suited for refluxing; its action is said to be perfect even when used with ether and petroleum ether. The figure under the heading "Extraction" shows how it should be set up for this purpose.

If there is danger that the reflux condenser may be clogged by a substance solidifying in it, a suitable volatile solvent is also placed in the flask. If, for example, iodine dissolved in boiling glacial acetic acid is allowed to act under a reflux, a portion of it often sublimes into the condenser before it is used up. To prevent stoppage and to aid in completely using up the iodine a dropping funnel is suspended in the condensing tube, into which a few drops of glacial acetic acid are allowed to flow from time to time to wash the iodine down. When Gottschalk[67] was oxidizing pentamethyl-benzene with nitric acid, he added enough benzene to the boiling mixture to wash back the hydrocarbons solidifying in the condenser.

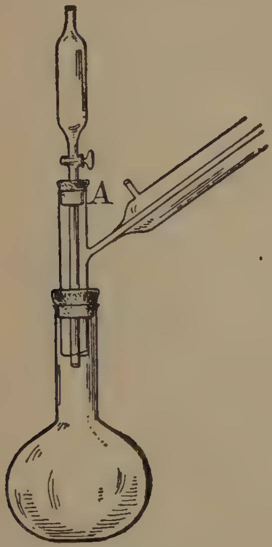

Fig. 35. Ascher's Reflux Condenser

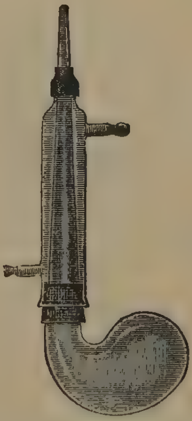

Fig. 36. Long-Neck Retort with Direct-Attached Condenser

If a gas is evolved while boiling under a reflux or if a current of gas is led through the contents of the flask, despite the best cooling some of the liquid will be carried away by it, corresponding to the vapor tension of the liquid. If, however, the gas stream, after leaving the condenser, is passed through water, the greater part of its burden will be retained by the water. For example, in the preparation of carbon tetrachloride by passing chlorine into boiling chloroform in the sunlight, the writer found that a considerable quantity of a heavy liquid mixture of chloroform and carbon tetrachloride gradually collects if the unabsorbed gas is passed through water.

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[67] Gottschalk, M., *Ber.*, **20**, 3287 (1887).

Technical experience shows clearly that the quantity of comparatively low boiling materials carried away because of vapor tension, by even a cooled current of gas, is not as inconsiderable as is usually assumed. Now-a-days, to obtain blast furnace coke, coal is coked in such a way, that the by-products which are formed can be collected. After the gas evolved has been freed from tar by cooling and of ammonia by washing with water, it is drawn (differing from the preparation of illuminating gas) through high boiling tar oils which remove the gaseous benzene from it, and many hundred thousand kilos of the latter, formerly lost, are recovered.[68]

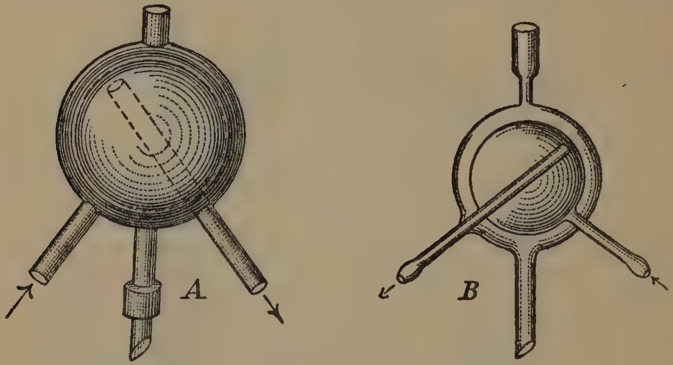

FIG. 37. SOXHLET'S BALL CONDENSER
A, metal; *B*, glass

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[68] A modified form of Liebig condenser, which is very efficient, may be readily constructed by selecting a condenser with a wide (15 to 20 mm.) inner tube and indenting it at frequent points along its length by heating small areas to dull redness and sucking these into semi-bulbs which extend slightly beyond the central axis of the tube. These indentations are preferably situated each at an angle of 120° in relation to its predecessor. Such a condenser is capable, for example, of condensing practically all of the bromine from the hydrogen chloride evolved from the bromination of acetyl chloride, provided the temperature of the cooling water be below 10°.—H. T. C.

The Liebig condenser which is somewhat inconvenient for refluxing, because of its length, may be replaced by the Walther condenser mentioned above, and also by the very handy Soxhlet ball-condensers. These are made so that one sphere has a smaller one fastened in it and a stream of cold water is run through the latter. Because of the excellent heat conductivity of metals, the Form A (fig. 37), which illustrates the metal condenser, is more efficient in heat transference than the Liebig condenser of poorly conducting glass. Therefore, the outer surface acts as an air condenser, which is not true of the Liebig condenser. They are now also made of glass.

DISTILLATION IN A CURRENT OF STEAM

Many substances which of themselves can hardly be volatilized without decomposing, may be distilled by a current of steam, and in many cases, this is the most convenient method of separating them from the other materials present. This is most easily accomplished by passing a current of steam through the liquid while it is heated on a double gauze (see the heading "Baths"), or on a water or sand bath. If the heating is omitted, too much water vapor condenses in the liquid.

The rapidity with which substances may be removed from their solutions by a current of steam depends, as does the extraction of liquids, much more than is ordinarily assumed, on the reaction and salt content of the solution. The writer saturated solutions from which materials are to be driven over by steam, with sodium chloride or a more soluble salt. This so accelerates the process that one liter of distillate will then contain as much as six times the quantity of organic materials. Auwers[69] states that trimethyl-succinic acid distils slowly with steam from an aqueous solution, but rapidly from one strongly acidified with sulfuric acid, a fact also observed by Königs.[70]

Steam is generated best in a metal boiler. If this is not available, a one or two liter glass flask is half filled with water, and several small pieces of zinc are put in, after adding a few drops of sulfuric acid. A slow evolution of hydrogen continues during the boiling, and in this way, a regular, smooth, long continued current of steam is obtained. If these additions are not made the water, as is well known, does not boil well, but bumps badly and consequently delivers a very irregular current of steam. Most metal steam generators require too much time to get up steam; during small distillations entirely too much water must be brought to a boil, and during long continued distillations, it is necessary to take the apparatus apart and refill it. These inconveniences are obviated in Reiser's steam generator (fig. 38). The apparatus is only about 5 cm. in diameter and the small quantity of water may be quickly converted into steam. The water to be evaporated is delivered continuously through a visible inlet *z* into a level tube *w*, so that the distillation may be continued as long as desired. The apparatus may be held in place by a clamp.

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[69] Auwers, K., *Ber.*, **28**, 265 (1895).

[70] Königs, Wilhelm, *Ber.*, **26**, 2338 (1893).

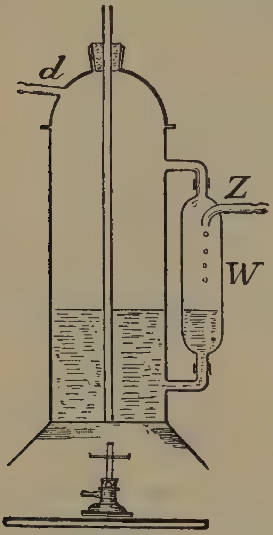

Fig. 38. Steam Generator (Reiser)

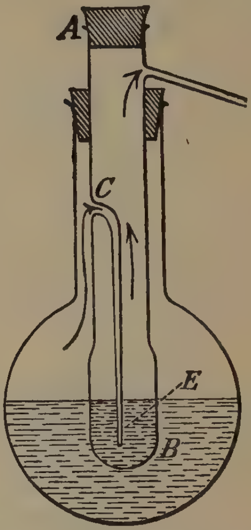

Fig. 39. Small Steam Distilling Apparatus (Pozzi)

If it is necessary to make frequent steam distillations of small quantities of liquids, as, for example, in preliminary tests to determine whether materials are sufficiently volatile in steam, the ingenious small apparatus devised by Pozzi[71] may be used advantageously.

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[71] Pozzi-Escott, *Bull. Soc. Chim.*, [3] **31**, 932 (1904).

The arrangement is clear from the illustration (fig. 39). The glass tube *AB* should be 14 to 18 mm. in diameter, and its lower flask-like bulb should have a capacity of 20 to 30 cc. The small tube, *CE*, is sealed in about 180 mm. from *A* at *C*, and *E* should be about 4.5 mm. from the bottom of the tube *AB*. Since the liquid on the inside of *AB* is at the temperature of boiling water, steam will pass through it without condensing.

Stoltzenberg[72] discusses the conditions of steam distillation as follows. The ordinary methods now in use have various disadvantages. Bumping and the frequent spraying of liquid into the distillate have often made necessary an apparatus inconvenient and time consuming to assemble and yet not satisfactory. His new steam inlet tube remedies these difficulties (fig. 40). It consists of a straight glass tube sealed at the bottom and having at its lower end a group of small bent tubes with fine openings. This offers the following advantages: in the first place, a large number of fine bubbles of steam issue simultaneously from the numerous fine openings. This increases its efficiency, *i.e.*, more of the steam is used up. Secondly, the steam issues into the liquid at right angles, its impetus is not upward, but toward the sides. This not only produces a more energetic mixing of steam and liquid, but, since each jet of steam forces liquid ahead of it, causes a vigorous circular movement of the

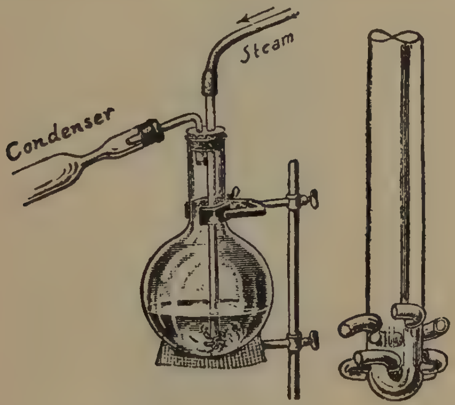

FIG. 40. STEAM INLET TUBE (STOLTZENBERG)

entire contents so that spurting over is eliminated. It is unnecessary to use a flask either with a contracted or a particularly long neck or one set at an angle. There is no bumping, so the flask need not be fastened tightly. Finally, the distillation takes less time since a more energetic current of steam than is customary, may be used. (This steam injector can also be used as a steam stirrer while dissolving salts, for stirring up slimy precipitates, etc., and may be operated with compressed air instead of steam.)

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[72] Stoltzenberg, H., *Ch. Zt.*, **32**, 770 (1908).

Larger laboratories can make use of Landolt's steam generator (fig. 41). This is a small, but complete steam boiler heated by gas. It delivers steam up to half an atmosphere super pressure and has many other uses. The writer has found it most satisfactory.

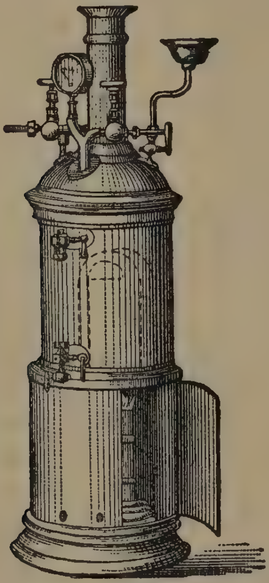

FIG. 41. STEAM GENERATOR (LANDOLT)

If it is necessary to steam distil products which are easily colored by oxidation, such as aromatic amino compounds, an atmosphere of carbon dioxide is used. Bechhold[73] recommends that the water furnishing the steam be previously saturated with hydrogen sulfide.

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[73] Bechhold, J., *Ber.*, **22**, 2378 (1889).

Schultz[74] has found it advantageous to add animal charcoal to liquids to be distilled in order to obtain uncolored products.[75]

DISTILLATION IN A CURRENT OF SUPERHEATED STEAM

Steam distillation is accelerated, and in many cases, may be accomplished only by the use of superheated steam. It is usually unnecessary to heat the material to be distilled, since the superheated steam will always keep the temperature up to the boiling point of the salt solution in the flask. If this is to be as high as possible, an indifferent salt such as sodium chloride, may be purposely added to the liquid to be worked up. The addition of such materials to raise the temperature of liquids to be heated by a current of steam is an old established practice in the ethereal oil industry.[76]

The writer superheats the steam by passing it through a copper spiral (fig. 42) having about 10 coils heated by a quadruple burner. The copper tube should be about 5 mm. in diameter, and the walls about 1.5 mm. thick and should have a projection soldered to it for convenience in fastening the stopper. The spiral is obtained by winding the copper tubing around a bolt about 3 cm. in diameter. To better conserve the heat, the spiral is surrounded by a shield which also supports it. The more distant connections of the apparatus may be of cork, even though the temperatures at even the most remote points, are too high for rubber. If the temperature is too high even for cork, asbestos pulp moistened with water glass may be used in its place.[77]

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[74] Schultz, Moritz, *Ber.*, **20**, 2721 (1887).

[75] The distillation in a current of steam of substances which are solid at the ordinary temperature is attended with danger if an ordinary Liebig condenser is employed, owing to the tendency of the inner tube to become plugged with solidified distillate, resulting in a violent disruption of the apparatus. In such a case the water jacket should be omitted and the condensation effected by running cold water over the receiving flask, which should be of large size in order to afford sufficient cooling surface. This method of cooling is really much more efficient than that involving a water jacketed condensing tube, and is recommended for all steam distillations.—H. T. C.

[76] Wagner, Rudolf von, *Chemical Technology*, translated by Crookes, W., New York (1892), p. 925.

[77] Pinnow, J., and Müller, E., *Ber.*, **28**, 150 (1895); Vorländer, D., and Schilling, R. von, *Ann.*, 310, 372 (1900).

Freundlich[78] has devised a steam superheater in which the burner both generates and superheats the steam (fig. 43). For this purpose, he solders into the cylindrical steam generator *A*, made of tin plate, a hollow cone containing the superheating coil *S*. *R* is the safety tube. The thermometer *T* indicates the temperature of the superheated steam which may soon exceed 400°, if a powerful enough burner is used. The non-superheated steam may be released into the air, after the distillation, by opening the pinch clamp, *Q*.

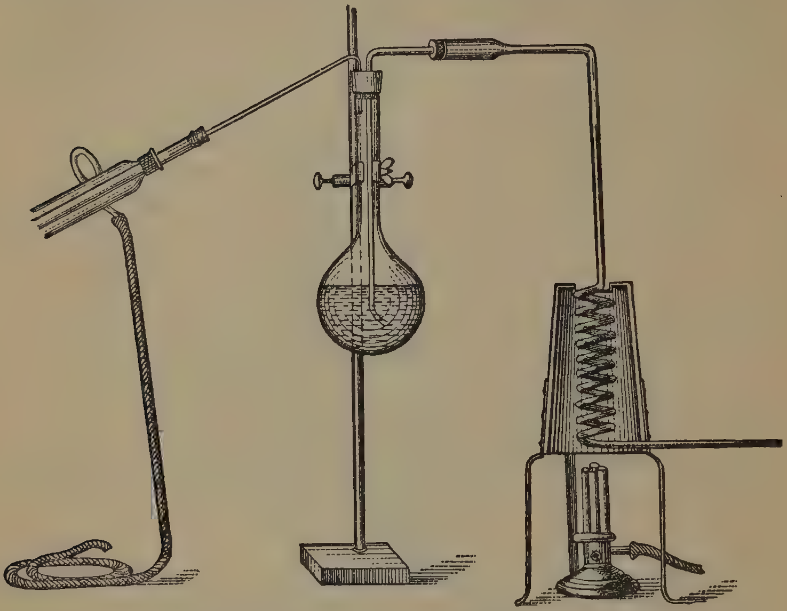

FIG. 42. DISTILLATION WITH SUPER-HEATED STEAM (LASSAR-COHN)

The slight bend (fig. 42) at the lower end of the tube through which the superheated steam is passed into the flask, prevents the spurting over of the liquid violently thrown back and forth by the steam. It is well to make the tube, whose bent end dips into the liquid to be distilled, of hard glass, which is less likely to break under these conditions than soft glass, even though, after long use, it becomes just as brittle as the latter.

Spurting over is ordinarily avoided by setting the flask at an angle

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[78] Freundlich, J., *Ch. Zt.*, **26**, 1084 (1902).

(fig. 44) but the writer has not found this satisfactory. This view is shared by Ziegler.[79] He believes that the ordinary thin walled round flasks should never be used in distillations with steam under pressure. If they are set upright, spurting and consequent contamination of the distillate are unavoidable. The long established custom of slanting the flask requires, as he points out, not only a double hole stopper, but also complicated bends in tubes and also two stands to make the apparatus fast. Despite these complications, because of the narrowness of the bent tubes, there is often choking, foaming, spurting over, and frequently the thin walled flask breaks. In Ziegler's flask (fig. 45) a divided current of steam is used. These flasks are made of thick walled, well annealed glass, and of such form and size that it is possible to distil, with the aid of high pressure steam, very difficultly volatile materials, and obtain pure distillates uncontaminated by spurting over. This operation, formerly requiring days, may be accomplished in a few hours. The steam injector of Stoltzenberg described above is also suitable for superheated steam.

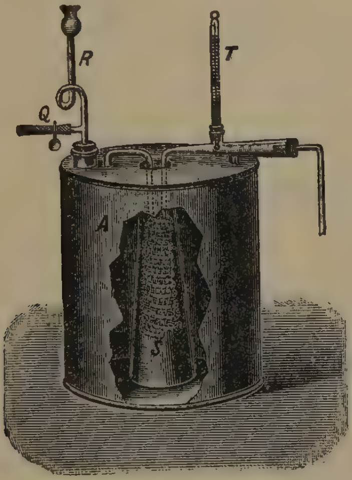

FIG. 43. COMBINED STEAM GENERATOR AND SUPER-HEATER (FREUNDLICH)

Ramdohr[80] was the first to point out, that, no matter how steam is heated, its temperature will always be above or below that of the boiling contents of the flask. A lasting coincidence of these two temperatures cannot be attained. If the entering steam is colder than the boiling liquid, or than the vapors arising from it, it will cool them, and condense a portion of them which must be revaporized by it later. Steam which is too hot may often decompose the boiling liquid or the vapors generated from it. His suggestions for avoiding these evils in factory practice cannot be carried over into laboratory procedure. In general, it is not necessary to worry too much about the temperature of the superheated steam, and care as to the degree of superheating is essential only when working with very sensitive substances. Thus, Salkowski[81] mentions that the skatole-carboxylic acid produced by putrescence, resinifies to a considerable extent if the steam is too greatly overheated when attempts are made to drive it over in this way.

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[79] Ziegler, Josef, *Ch. Zt.*, **21**, 97 (1897).

[80] Ramdohr, L., German patent 5315 (1878); *Chem. Industrie*, **2**, 257 (1879).

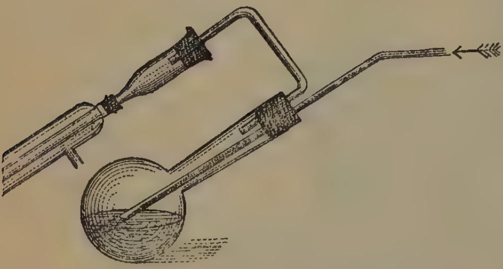

Fig. 44. Steam Distillation with Inclined Flask

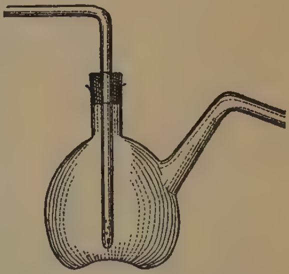

Fig. 45. Flask for Steam Distillation (Ziegler)

FRACTIONAL DISTILLATION IN A CURRENT OF STEAM

Rasinski[82] carried out experiments on fractional steam distillation, but had little success with the petroleum hydrocarbons with which he worked. Lazarus[83] later resumed these experiments after Naumann had shown that liquids not miscible with water always distil in a current of steam at temperatures below the boiling point of water. He fractionated the mixture in a gentle current of steam, and collected the distillate in two to three parts. He obtained from a mixture of 25 cc. toluene and 25 cc. nitrobenzene the result shown in table 2. There were recovered 22.5 cc. of toluene and 23 cc. of nitrobenzene. This method did not give a sharp separation of benzene and toluene, and accordingly, as Lazarus stated, is of use only with liquids, whose boiling points are not too close together.

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[81] Salkowski, E., *Z. physiol. Ch.*, **9**, 493 (1885).

[82] Rasinski, F., *J. pr. Ch.*, [2] **29**, 39 (1884).

[83] Lazarus, M. J., *Ber.*, **18**, 577 (1885).

Tiemann and Krüger[84] in their extensive investigation of the preparation of the pure aroma of the violet, used methodical fractional distillation in currents of steam.

Hardy,[85] reviewing the published data, drew the following conclusions as to the separation, by fractional distillation with steam, of substances such as limonene and citral, limonene and eugenol, cineol and citral, chloroform and carbon tetrachloride, benzene and acetic acid. He found: (1) steam distillation, in many cases, separates the components of a mixture of volatile substances better than ordinary distillation with dry heat. If the materials to be separated boil far below 100°, steam distillation is of little value; (2) the effect of fractionating columns is considerably less than in the ordinary procedure; (3) the rate of distillation has little influence on the result, indeed, in many cases, it is advantageous to pass the steam through the mixture as rapidly as possible; (4) particularly good results may often, though not always, be obtained, by steam distilling under reduced pressure.

TABLE 2

Results of Lazarus' distillations

FRACTION	TEMPERATURE	VOLUME	TOLUENE	NITROBENZENE
	degrees	*cc.*	*cc.*	*cc.*
1	90–95	21.0	19.0	
2	95–98	6.0	3.5	
3	98	23.0		23.0

DISTILLATION IN A CURRENT OF ALCOHOL OR ETHER VAPOR

Many substances are volatilized just as well by the vapors of other liquids as they are by water vapor, and this behaviour provides a very practicable means of separating and obtaining them. Bunzel[86] believes that the distillation with alcohol vapors is the best method for preparing pure α-pipecolin, and Askenasy and Victor Meyer[87] state that perfectly pure nitropropylene is most easily obtained if it is quickly distilled in a current of ether vapor. Acetonyl acetone is also volatile to a considerable extent in ether vapor.[88] If the preparation of such materials involves extraction of their solutions with ether, and if this extraction is repeated several times, the same ether which had already served this purpose and had been recovered by distillation, would, of course, be used. Thus the loss of material may satisfactorily be reduced.

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[84] Tiemann, Ferd., and Krüger, Paul, *Ber.*, **26**, 2677 (1893).

[85] Hardy, H., and Richens, B., *Analyst*, **32**, 197 (1907).

DRY DISTILLATION

Metal apparatus should be used when dry distilling large quantities of materials, because glass conducts heat too poorly, and consequently, the yields are much lower.

If organic bodies are subjected to dry distillation, deep seated decompositions naturally occur. Up to 1830, the knowledge of the reactions had hardly extended beyond the fact that water, tarry oils, and solid residues are obtained. By that time, it was recognized, that organic substances are thus decomposed into simpler materials such as water, carbon dioxide, carbon monoxide, solid, liquid and gaseous hydrocarbons and charcoal. On the other hand, Saussure[89] found that naphthalene is formed when alcohol or ether vapors are passed through hot tubes.

In 1832 Liebig and Dumas found water, carbon dioxide and acetone as the products of the distillation of acetates, and Persoz[90] discovered the formation of carbon dioxide and methane when the same salts are decomposed under different conditions; reactions which are now represented:

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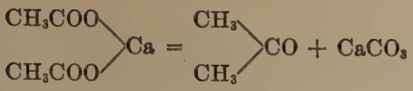
[86] Bunzel, Hugo, *Ber.*, **22**, 1053 (1889).

[87] Askenasy, Paul, and Meyer, Victor, *Ber.*, **25**, 1702 (1892).

[88] Knorr, Ludwig, *Ber.*, **22**, 169 (1889).

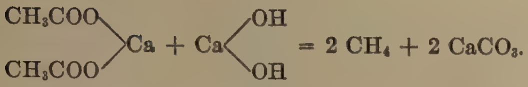
[89] Saussure, Th., *Gehlen's Journ.*, **4**, 69, 79, (1807); see also Reichenbach, *Schweiggers Journ.*, **61**, 191 (1831); see also *Gmelin, Handbuch d. Chemie* 4th ed., Heidelberg (1848) vol. 4, p. 532, ,552.

[90] Persoz, J., *Introduction a l'etude de la chimie moleculaire*, Paris, 1839; see also Pelouze, J., and Millon, E., *Ann.*, **33**, 182 (1840).



$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>Ca = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + CaCO_3$$

and



$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!\!>Ca + Ca<\!\!\begin{matrix}OH\\OH\end{matrix} = 2\,CH_4 + 2\,CaCO_3.$$

After Mitscherlich,[91] in 1833, had shown that the dry distillation, particularly of calcium benzoate with an excess of quick lime, produces equal volumes of benzene and carbon dioxide—both measured in the gaseous state—$C_6H_5-COOH = C_6H_6+CO_2$, a result which is obvious from our present molecular theory, and after Piria[92] had obtained benzaldehyde by distilling calcium benzoate with calcium formate, this method became of great interest and is now a frequently used laboratory procedure.[93]

The general method of dry distillation is to distil small quantities of the substance, from small retorts, from bulb tubes, or simply from hard glass tubes heated in combustion furnaces. Sand or similar substances are mixed with the material to be distilled, to avoid the possible cessation of the reaction,[94] observed, for example, by Zincke when heating a mixture of trichlor-m-hydroxy-benzoic acid with lime; and to prevent undesirable sintering. Wieser[95] mixed guiac gum with particles of pumice. Jacobsen[96] made the valuable suggestion of adding iron filings to the materials to be distilled, such as calcium salts. In this way, the difficulties arising from the poor heat conductivity and from the sintering of the lime mixtures are obviated. The regular distillation is said to be completed at comparatively low temperatures and it is also claimed that the glass retorts are always fit to be used for new operations. This is the first serious attempt to modify the process so as to increase the low heat conductivity of the salts and thus avoid the overheating of the outer portions. The suggestion has met with little approval because, under these conditions, iron may easily reduce many salts.[97]

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[91] Mitscherlich, E., *Ann.*, **9**, 43 (1834).

[92] Piria, R., *Ann.*, **100**, 105 (1856).

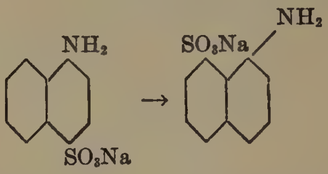
[93] Haber, F., *Ber.*, **29**, 2691 (1896). Haber published a theory of the pyrogenetic reactions of aliphatic hydrocarbons with reference to the older assumptions.

[94] Zincke, Th., *Ann.*, **261**, 241 (1891).

[95] Wieser, H., *Monatsh.*, **1**, 595 (1880).

[96] Jacobsen, Oscar, *Ber.*, **12**, 429 (1879).

This problem was solved much later by a patented process which attempted to improve the yield of products obtained by the dry heating of a salt. For instance: if a salt of naphthionic acid, preferably the potassium or sodium salt, is heated for some time at 200 to 250°, it is transformed to the salt of the isomeric 1,8-naphthylamine-sulphonic acid. This fact was published in 1890.[98]



The procedure is as follows: sodium naphthionate is heated in an oil bath at 220 to 240° in a closed vessel provided with a stirrer, until the transformation is complete, as shown by the slight solubility of the product in water, and by the disappearance of the intense blue fluorescence of the dilute solution of the fused salt. The alkali salts of the new acid are slightly soluble in water, in contrast to those of the naphthionic acid. It is said to be advisable to pass a slow current of an indifferent gas, such as carbon dioxide, through the mass during the whole operation, and even during the cooling. This removes any naphthalene present in the original materials. The transformation occurs at a correspondingly lower rate at a lower temperature.

In 1892,[99] it was made known that even though the conditions laid down in the patent were closely adhered to, it was not possible to raise the yield of the 1,8-naphthylamine-sulfonate above 40 per cent. The chief reason was that the pulverized sodium naphthionate, being a poor conductor of heat, was not thoroughly heated through, even though well stirred, and the various parts of the salt were not heated uniformly. A part of the naphthionate, consequently, is completely decomposed, and if even naphthionate free of naphthylamine is used, there are obtained as by-products, α-naphthylamine, dinaphthylamine, smears, tar and coke. The subsequent purification of the 1, 8-naphthylamine-sulfonic acid is much more difficult if these by-products are present. The formation of these is practically avoided if a diluent boiling at the temperature required for the transformation is used. Naphthalene boiling at 218° was found very suitable, since this temperature almost coincides with the transformation temperature. Only traces of α-naphthylamine are formed when the salts of naphthionic acid are heated in boiling naphthalene, and these are easily removed. The other by-products mentioned above are not formed at all. The resulting 1,8-naphthylamine-sulfonate is of greater purity, and the yield is almost quantitative. The improved procedure is: 20 kgm. of well dried and sifted sodium naphthionate is added to 40 to 60 kgm. fused naphthalene, in a kettle provided with a stirrer and a reflux tube, and heated to the boiling point of the naphthalene. The reaction mass is kept at this temperature until the transformation is complete, usually requiring two to three hours. After cooling somewhat, the mass is treated with water, and the naphthalene recovered by steam distillation. The residue is diluted with water to 150 to 200 liters, neutralized by the addition of soda lye or sodium carbonate, brought to a boil, filtered from the very small quantity of pulverulent dirt, and the sodium naphthylamine sulfonate precipitated by the addition of salt. Relatively small quantities of salt suffice to almost completely precipitate the new sodium salt which is difficultly soluble. The yield is excellent and the immediate product very pure.

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[97] It is difficult to see how particles of iron separated from each other by poorly conducting material can carry much heat.—E. E. R.

[98] Ch. Fab. Grünau, Landshoff and Meyer, German patent 56563 (1890); Fr. II, 269.

[99] Bayer & Co., German patent 72833 (1892), Fr. III, 427.

This means of increasing the yield should be capable of frequent application in the laboratory. Salts may be heated uniformly in an indifferent medium selected from the hydrocarbons, such as phenanthrene etc., and if a reflux condenser is used, temperatures up to the boiling point of mercury are available. Furthermore, the flasks used in this process do not suffer, whereas they are usually ruined by other methods of heating dry salts in them.

As a rule, dry distillations, not using this aid, are very tedious because good yields may only be obtained by the former procedures when small quantities are distilled at one time, since the interiors of larger masses are heated through at the expense of overheating the outer portions. The writer believes that if the process described proves of wide applicability, the preparation of aldehydes, ketones and similar materials, will again be made by dry distillation which has now been largely abandoned in the laboratory because of its inconvenience and poor yields.

The shape of the usual high, lengthy retort bulbs contributes to the overheating of salts. According to Mager,[100] the yields may be improved when glass retorts holding 10 to 15 grams are used, by surrounding them with a removable iron jacket which transmits the heat to them more uniformly. In case the use of an indifferent material is not feasible, a remedy for these evils must be sought elsewhere. This may be achieved, for example, by spreading the salt mixture to be distilled, on a plate, provided the products of distillation may still be collected. The ter Meer[101] retorts attempt to meet these requirements. Thus, 20 distillations of 50 grams portions of a mixture of equal parts of calcium butyrate and formate, produced 270 grams of crude butyraldehyde. Lieben[102] obtained about 250 grams crude aldehyde from 100 distillations of 10 gram portions of the same mixture. The arrangement of the retort if made clear by figure 46 (one-fourth natural size).

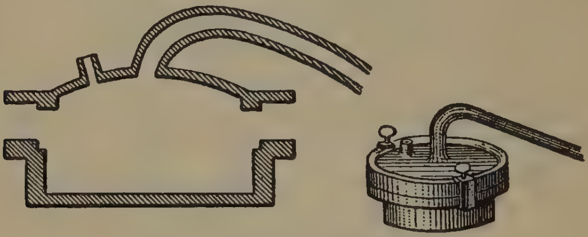

FIG. 46. TER MEER RETORT

Wohl and Neuberg[103] recommend that a Papin cup be used as a metal retort. Its top may be made tight by tamping asbestos cord into the anulus. It is heated by two groups of 10 burners each.

Pauly[104] states, that if great losses are to be avoided, metal vessels must be used for the distillation of materials which do not decompose easily, and which will not endure long overheating. His apparatus which he has thoroughly tested is as follows: A copper cylinder,

[100] Mager, H., Dissertation, Leipzig, 1890.

[101] ter Meer, E., *Ber.*, **9**, 844 (1876).

[102] Lieben, A., and Rossi, A., *Ann.*, **158**, 147 (1871).

[103] Wohl, A., and Neuberg, L., *Ber.*, **32**, 1353 (1899).

[104] Pauly, Hermann, and Neukam, Karl, *Ber.*, **40**, 3495 (1907).

9 cm. high, 4 cm. internal diameter, and 2 mm. walls, with a hard bottom soldered in, carries a 1.5 cm. reinforcement around its upper edge, so that it is 5 mm. wide (fig. 47). The latter is turned at exact right angles to the length of the cylinder and is highly polished. The reinforcement is threaded so that a cover of bronze may be screwed down tightly. Its inner surface is turned vertically to the threads, and polished so that the edge fits tightly when it is drawn up, thus insuring an air tight seal. The cover has a cylindrical shoulder with a stuffing box through which a closely fitting stout glass tube carrying a sealed-on receiver may be inserted in the 11 to 12 cm. opening. The closing of the joints needs special attention, and asbestos is very suitable. The stuffing box may easily be made tight by thick asbestos cord; the cylinder and cover are closed by a well fitting asbestos ring about 1 cm. wide which is prepared as follows: after it has been fitted as well as possible, both its sides and edges are ground with the finest emery paper until perfectly smooth. It is then thoroughly moistened with water, put into the cover, and the cylinder turned up tight repeatedly by hand while the asbestos ring is turned over several times until it shows fine polished impressions on both sides. It is then allowed to dry, but without heating, so that it remains soft. Before use, the ring and likewise the stuffing box cord, is rubbed thoroughly, but as sparingly as possible, with a viscous oil which has been heated to a high temperature. It should be practically non-volatile, even when highly heated, but should only

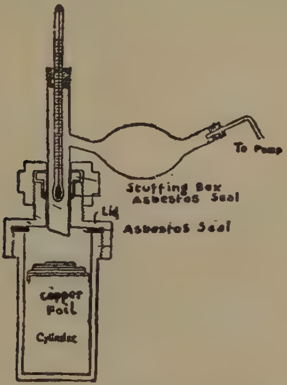

Fig. 47. Metal Apparatus for Dry Distillation (Pauly)

coke. This oil is on the market for the machine trade, but should not be a petroleum product. A water pump will easily give a vacuum in this apparatus, of at least 20 to 25 mm., which will remain constant even at higher temperatures. The inner chamber of the cylinder is filled with copper foil ("copper foil electrolytic" 0.1 mm.) 6 cm. wide, bent back and forth and standing upright so as to produce small air spaces 1 to 2 mm. wide. The material is well mixed with $1\frac{1}{2}$ to 2 times the quantity of copper powder and the mixture packed in the air spaces. The heating is done in oil or metal baths. The apparatus shows very little wear and even at higher temperatures, the ground surface remains smooth and tight and the inner walls hardly oxidize. The yields fell off when more than 3 gm. were worked up in glass vessels, while this apparatus permitted charges of 20 to 30 grams and the period of heating, which plays a great rôle when glass vessels are used, may be considerably shortened.

GENERAL BEHAVIOR OF SALTS WHEN DRY DISTILLED (ALSO IN VACUO)

Although well dried calcium salts are usually dry distilled to eliminate the COO of the carboxyl groups of the acid, this practice is based more on custom than on scientific considerations. It is not necessary to convert comparatively simple acids into their calcium salts, but they may be directly mixed with powdered slaked lime. Mitscherlich[105] did this when he prepared benzene from benzoic acid. Marignac[106] describes the production of benzene from phthalic acid as follows: when naphthalene acid hydrate (now called phthalic acid) is heated with an excess of slaked lime it loses carbon dioxide which combines with the lime, while quite pure benzene is formed,

$$C_6H_4(COOH)_2 = C_6H_6 + 2\ CO_2$$

The thermal decomposition of the calcium salts of fatty acids produces the corresponding ketones, together with calcium carbonate. The latter decomposes at about 500° into calcium oxide and carbon dioxide. The quick lime has a very harmful action on the ketone formed (say acetone) since, according to Becker,[107] it condenses 10 to 20 per cent of the ketone if it remains in contact with the acetone vapors for only a few seconds. He, therefore, believes that it is very necessary to prevent the formation of the quick lime. This may be done by completely neutralizing the salt of the fatty acid, in this case calcium acetate, and then decomposing it in a current of dry carbon dioxide, or a gas containing a large proportion of it. No quick lime forms, even though the calcium salt of the fatty acid may be overheated locally. The writer believes that these facts should be considered in all dry distillations, and this is the explanation why barium salts give better yields than calcium salts.

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[105] Mitscherlich, E., *Ann.*, 9, 39 (1834).

[106] Marignac, J. C. G. de, *Ann.*, 42, 217 (1842).

[107] Becker, J., German patent 170533 (1903); Fr. VIII, 33.

Krafft's studies, to be discussed later, show why, in most cases, barium salts are preferable to calcium salts. Mixing well dried calcium carbonate (or barium carbonate) with the calcium (or barium) salt of the organic acid is said to improve the yield. Thus Döbner[108] found that β-vinylacrylic acid is best transformed into hydrocarbons by mixing 10 grams of it with 30 grams of anhydrous barium hydroxide, and distilling the mixture from a fractionating flask. The heating should be very gradual. The yield of liquid hydrocarbons condensed by ice was 30 per cent.

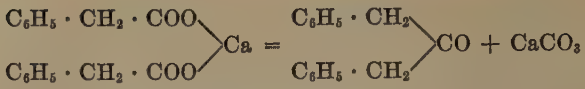
Krafft[109] recommends that barium instead of calcium salts be used for the preparation, particularly of aldehydes, from acids of high carbon content, whose corresponding aldehydes would, therefore, not be too volatile. The barium salt of the fatty acid is mixed with twice its weight of barium formate. The calcium salts are not so well suited for the preparation of aldehydes and ketones, partly because of the lower stability or formation tendencies of the calcium carbonate at high temperatures as compared with the much more stable barium carbonate, and partly because they are more difficult to fuse. He advises that the intimate mixture of the barium compounds should be dry distilled at a pressure of about 8 to 15 mm., (see the following heading "Distillation under Reduced Pressure"), from flat retorts which permit immediate escape of the vapors. The temperature should be raised very carefully.

The following statements are supplementary to the above. Wieland[110] found that a vacuum distillation of calcium phenylacetate produced 60 to 70 per cent of the theoretical yield of dibenzyl ketone.

[108] Döbner, O., *Ber.*, **35**, 2133 (1902).

[109] Krafft, F., *Ber.*, **12**, 1664 (1879); **15**, 1711 (1882).

[110] Wieland, Heinrich, *Ber.*, **37**, 1143 (1904).



$$\left.\begin{array}{l} C_6H_5 \cdot CH_2 \cdot COO \\ C_6H_5 \cdot CH_2 \cdot COO \end{array}\right\rangle Ca = \left.\begin{array}{l} C_6H_5 \cdot CH_2 \\ C_6H_5 \cdot CH_2 \end{array}\right\rangle CO + CaCO_3$$

Stobbe[111] states that the barium salt gives only a 50 per cent yield. Apitzsch[112] found that 83 per cent of the theoretical yield may be obtained without distilling in vacuo, if 500 grams of calcium phenylacetate is dried in flat porcelain dishes at 150 to 160° for about an hour, until the salt forms a viscous mass which is vitreous and brittle when cold. About 450 grams of the coarsely pulverized, dried salt is directly heated (in two portions) by means of a burner, in non-tubulated retorts holding about 300 cc. and made of combustion tubing. They are provided with short air condensers and the heating is continued until tarry products only are passing over. The crude distillate amounts to about 300 grams. This is taken up with an equal volume of ether, well dried with sodium sulfate, the ether distilled off, and the residue fractionated two or three times. About 240 grams pure ketone is obtained.

Vorländer[113] dry distilled in 15 to 20 gram portions, at a pressure of 15 to 20 mm., barium diphenylacetate dehydrated at 150 to 160°, hard glass retorts placed in an iron dish and surrounded by iron filings. A slightly reddish oil passed over first and later, a product that crystallized immediately in the neck of the retort. After cooling, the solid product (about 5.5 grams) is separated from the liquid (about 7 grams), and the former is recrystallized from boiling acetone. In this way, tetraphenyl-allene was obtained. The formation of this hydrocarbon may be explained by assuming that, in vacuo, tetraphenylacetone is formed in the normal way from a part of the salt, but when distilled the ketone loses water, forming tetraphenylallene.

$$\begin{array}{c} (C_6H_5)_2CH\text{—}CO\text{—}O\text{—}Ba\text{—}O\text{—}OC\text{—}CH(C_6H_5)_2 \\ \downarrow \ (-\ BaCO_3) \\ (C_6H_5)_2CH\text{—}CO\text{—}CH(C_6H_5)_2 \\ \downarrow \ (-\ H_2O) \\ (C_6H_5)_2C{=}C{=}C(C_6H_5)_2 \end{array}$$

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[111] Stobbe, H., *Ann.*, **308**, 175 (1899).

[112] Apitzsch, Hermann, *Ber.*, **37**, 1429 (1904).

[113] Vorländer, D., and Siebert, C., *Ber.*, **39**, 1027 (1906).

Groussilliers[114] states that acetone may be prepared on a large scale by dry distilling barium acetate, or by distilling calcium acetate with superheated steam. The writer believes that superheated steam with its fluctuating temperature is a much poorer method of keeping the temperature constant, than is the use of boiling hydrocarbons so thoroughly discussed above. To avoid the decomposition of the acetone which is formed by heating calcium acetate, because of overheating on the hot walls of the vessel heated to a dull red, Wenghöffer[115] recommends that a solution instead of the dry salt be placed in the decomposition apparatus. The steam formed by the rapid heating immediately carries the acetone over with it. He directs that 1000 kgm. of a solution of calcium acetate, containing 220 kgm. of the salt, be run gradually into the decomposition vessel and heated until no more ketone forms. He obtained 830 kgm. of distillate containing more than 6 per cent acetone. From 500 liters of water and 500 kgm. of acetate treated in the same way the yield was 620 kgm. of distillate containing 18.5 per cent acetone.

It is not necessary to actually prepare the calcium acetate, but it is possible to make acetone[116] by filling the distillation bulb with a porous material, such as pumice, to which calcium acetate has been added. As soon as the acetone begins to distil, acetic acid vapor is run into the body of the retort, and combines with the calcium carbonate present, and the heat decomposition produces more acetone. It is claimed that a small quantity of calcium carbonate can transform any quality of acetic acid vapor into acetone.

The rather widespread use of soda lime in place of lime alone in dry distillations, cannot be highly recommended. Thus Gräbe[117] says that even though Bamberger could not obtain β-phenylnaphthalene by heating chrysoquinone with soda lime, as he himself had done, his failure was of little significance, since frequently, in such reactions, the quality of the soda lime has a decisive influence. Soda lime is such an uncertain mixture that its composition may vary within wide limits.

It may also be pointed out, that the dry distillation of different salts derived from the same acid do not always result in the same product. Thus Meyer and Hoffmeyer[118] obtained xanthone by the distillation of hydrofluoranic acid with lime, but an entirely different derivative of this acid was formed when barium hydroxide or soda lime were employed. Dale[119] states that azelaic acid, if heated with barium hydroxide, produces a mixture of materials from which heptane may be isolated, so that this may be considered as a method of preparing this hydrocarbon. However, Dale and Schorlemmer[120] found that an inseparable mixture of materials resulted when this acid was heated with lime.

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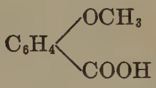
[114] Groussilliers, H. de, German patent 40982 (1886); *Ber.*, R, **21**, 111 (1888).

[115] Wenghöffer, L., German patent 144328 (1902); Fr. VII, 18.

[116] Société Pagés Camus et Cie, French patent 361379, *Ch. Zt. Rep.*, **30**, 248 (1906); German patent 30248, Fr. IX, 56.

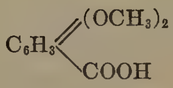
[117] Gräbe, C., *Ber.*, **27**, 952 (1894).

Position isomerism also makes its effect felt here. Hübner[121] investigated the dry distillation of calcium salts of many acids, from this point of view, and found that esters of the acids resulted if the latter contains a methoxy group para to the carboxyl, as in anisic acid



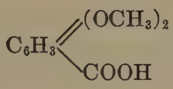
$$C_6H_4{<}^{OCH_3}_{COOH}$$

or in veratric acid



$$C_6H_3{<}^{(OCH_3)_2}_{COOH}$$

If, however, the methoxy groups are in the meta position, as in dimethyl-α-resorcylic acid,



$$C_6H_3{<}^{(OCH_3)_2}_{COOH}$$

no ester is formed. While this observation applies only to materials easily obtainable by other methods, the application of the following patent[122] to other suitable ring complexes, may lead to the preparation of many new nitriles and corresponding acids.

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[118] Meyer, Richard, and Hoffmeyer, Hermann, *Ber.*, **25**, 2121 (1892).

[119] Dale, R., *Ann.*, **132**, 247 (1864).

[120] Dale, R., and Schorlemmer, C., *Ann.*, **199**, 149 (1879).

[121] Hübner, E., *Monatsh.*, **15**, 719 (1894).

[122] Cassella & Co., German patent 92995 (1896); Fr. IV, 611.

If salts of naphthylamine sulfonic acids are dry distilled with potassium cyanide, they show a behavior that varies with their structure. Naphthionic acid decomposes, splitting off naphthylamine; one of the β-naphthylamine sulfonic acids exhibits an analogous behavior, likewise $\alpha_1\beta_1$- and $\alpha_1\alpha_4$-naphthylamine sulfonic acids. Surprisingly enough, several other acids yield a distillate rather rich in aminonaphtho nitriles, which have not been prepared by other methods. When these were saponified, they yielded new aminonaphthoic acids. They are best prepared by thoroughly mixing, say, one part of sodium naphthylamine sulfonate with 1.2 parts finely powdered potassium cyanide or potassium ferrocyanide, and distilling from an iron retort. The nitriles pass over as yellowish oils which soon solidify and are easily obtained pure by recrystallization from alcohol. Thus $\alpha_1\alpha_3$-amino-naphthonitrile forms reddish brown needles, $\alpha_1\beta_3$-amino naphthonitrile yellow needles, and so on. Lellmann and Reusch[123] obtained the desired ortho cyanquinoline by distilling, under a few millimeters pressure, sodium orthoquinoline sulfonate with cyanide.

There are, however, many other cases of dry distillation in which the sodium or potassium salts are better than the alkali earth compounds. For example, Grosjean[124] thoroughly mixed two parts of the barium salt of undecylenic acid, dried at 120°, with one part pulverized sodium ethylate, and distilled the mixture at a pressure of 50 mm., from a hard glass retort, and obtained 50 per cent of the theoretical yield of decylene.

Dry silver salts are also frequently distilled, and Kachler[125] has even attempted to formulate a general decomposition equation for the course of this reaction in the case of silver salts of the fatty acids. Königs and Körner[126] also recommend the distillation of silver salts in many cases when it it desired to split out carbon dioxide. This is of particular advantage over the usual distillation of acids or their calcium salts with bases, if, in addition to the carboxyl group, strongly acid hydroxyl groups are also present, as for example in the aromatic oxyacids. When they distilled hydroxy-cinchoninic acid with bases, charring occurred, but when they heated 5 grams of the silver salt,

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[123] Lellmann, Eug., and Reusch, H., *Ber.*, **22**, 1391 (1889).

[124] Grosjean, L., *Ber.*, **25**, 478 (1892).

[125] Kachler, J., *Monatsh.*, **12**, 339 (1891).

[126] Königs, Wilhelm, and Körner, Georg, *Ber.*, **16**, 2153 (1883).

$C_9H_5(OH)NCO_2Ag$, in a combustion tube in a current of carbon dioxide, they obtained, with little charring, in addition to quinoline, 2 grams hydroxyquinoline, $C_9H_6(OH)N$.

Bamberger[127] produced isocoumarin from the silver salt of isocoumarin-carboxylic acid by mixing the well dried silver salt with twice its weight of powdered clay tile and distilling the mixture from a small glass retort at the lowest possible temperature, in portions each containing 2.5 grams of the salt. He found there was no advantage in working in a vacuum. He used the salt after he was convinced that simply heating the acid to split out the carbon dioxide was not a feasible method of preparation.

Pechmann[128] distilled the mercurous salt of coumalinic acid, since the dry silver salt was not available, and he worked with 20 gram portions in a small tubulated retort, in a current of hydrogen. The yield of coumalin was 30 per cent of the theory, in addition to coumalinic acid and mercury. Wallach[129] observed that a considerable quantity of a yellowish material was formed in addition to anhydro-fenchocarboxylic acid when α-fenchocarboxylic acid was dry distilled. This material is the chief product of the distillation of lead fenchocarboxylate and was shown to be an isomer of anhydro-fenchocarboxylic acid. On the other hand, the sodium or copper salt yields entirely different distillation products. Later, he obtained carbofenchonone from the lead salt.[130]

Zelinsky[131] found that the dry distillation of calcium hexahydrobenzoate with sodium methylate produced a mixture of dihydro- and tetrahydrobenzene. This agreed with the observations of Mai,[132] who found with the higher fatty acids that, although their barium salts mostly produced ketones when distilled with soda lime, when sodium methylate was used instead of the latter, in vacuo, excellent yields of the hydrocarbons resulted.

The foregoing might give the impression that the dry distillation of salts of organic acids with inorganic bases only, would yield definite anticipated products. This generally accepted idea is too limited, as may be seen from a method published by Tschugaeff[133] for preparing unsaturated hydrocarbons by dry distilling the esters of xanthogenic acid. These esters, having a general formula, $C_nH_{2m-1}O\text{-}CS\text{-}SR$, in which R signifies any alcohol radical, are easily obtained with the aid of carbon disulfide. (The reaction seems to proceed most easily when $R = CH_3$). If they are distilled at ordinary or slightly diminished pressure, they usually decompose, primarily in accordance with the following equation:

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[127] Bamberger, Eug., and Frew, William, *Ber.*, **27**, 207 (1894).

[128] Pechmann, H. von, *Ann.*, **264**, 305 (1891).

[129] Wallach, O., *Ann.*, **300**, 300 (1898).

[130] Wallach, O., *Ann.*, **315**, 275 (1901).

[131] Zelinsky, N., and Gutt, J., *Ber.*, **41**, 2074 (1908).

[132] Mai, J., *Ber.*, **22**, 2133 (1889).

$$C_nH_{2m-1}O - CS - SR = C_nH_{2m-2} + CSO + R\text{—}SH$$

and with a side reaction:

$$C_nH_{2m-1}O - CS - SR = C_nH_{2m-2} + CS_2 + ROH$$

Both reactions produce an unsaturated hydrocarbon C_nH_{2m-2}, which may easily be freed from by-products containing sulfur, by distillation over metallic sodium, if need be. The decomposition proceeds easily and at comparatively low temperatures. The immediate product is pure, and the yields are usually satisfactory.

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[133] Tschugaeff, L., *Ber.*, **32**, 3333 (1899).

CHAPTER IV

DISTILLATION UNDER REDUCED PRESSURE AND IN VACUO

One of the most fruitful advances developed by modern chemical technique is the use of high vacua. The pressures obtainable with a water pump[1] are frequently no longer sufficient. The boiling point of most materials is lowered 100° or more below that shown in a vacuum produced by a water pump, at the vanishingly small pressures which are easily available with mercury pumps, mechanical pumps running in oil, or by the Dewar process using charcoal cooled with liquid air. In this way, decompositions during distillation may be avoided, which were inevitable at the pressures attainable with the ordinary water pump. Thus inosite, $C_6H_{12}O_6$, boils without decomposition at 319° in vacuo, whereas, it chars like a sugar when heated in the air. This compound, found in the heart muscles of animals, was long considered a sugar, but is now known to be a benzene derivative.

It is remarkable[2] that ordinary flasks and retorts, if not too large[3] and thin walled, may be used for vacuum distillations, and the air may be removed from them to within a few millimeters pressure, or even completely, and yet they are practically never crushed by the external atmospheric pressure. Retorts and flasks larger than about 0.5 liter should not be used, because they almost always break.[4] Thus ordinary glass apparatus may be used for these distillations, but modified forms suitable for this special purpose, will be discussed. Such distillations should never be made over a free flame, but baths as shown in figure 48 should always be used. In place of rubber stoppers, well bored soft corks may be used. After the apparatus has been assembled, these should be coated with collodion to insure tight joints.

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[1] The principle of the Bunsen water air pump in which falling water drags air with it was applied in the very early Spanish bellows used in the iron industry.—Lassar-Cohn, *Chemie im täglichen Leben*, Leipzig, 10th ed., p. 281.

[2] Not so remarkable, when it is considered that the reduction of the internal pressure, from the "vacuum" afforded by a water pump to the absolute vacuum produced with the aid of charcoal cooled by liquid air, corresponds with a relative increase in external pressure of only about 1 per cent.—H. T. C.

[3] Lunge, G., and Neuberg, O., *Ber.*, **24**, 729 (1891).

[4] The thick-walled Pyrex flasks of 12-liter capacity may be employed with perfect safety for the vacuum distillation of materials boiling up to 200° under reduced pressure, employing a free flame under a single wire gauze.—H. T. C.

One of the chief difficulties attending this operation has been the violent bumping of the liquids so that they were easily spurted into the condenser from the flasks in which they were boiling. Anschütz[5] was justified in pointing out, in his fundamental discussion of this subject, that the discovery of Dittmar in 1869 of a method of avoiding this, was responsible for the general adoption of this type of distillation. Dittmar's procedure was simply to draw a continuous current of dry gas through the boiling liquid during the distillation. This idea was adapted from that of Pellogio[6] who recommended this

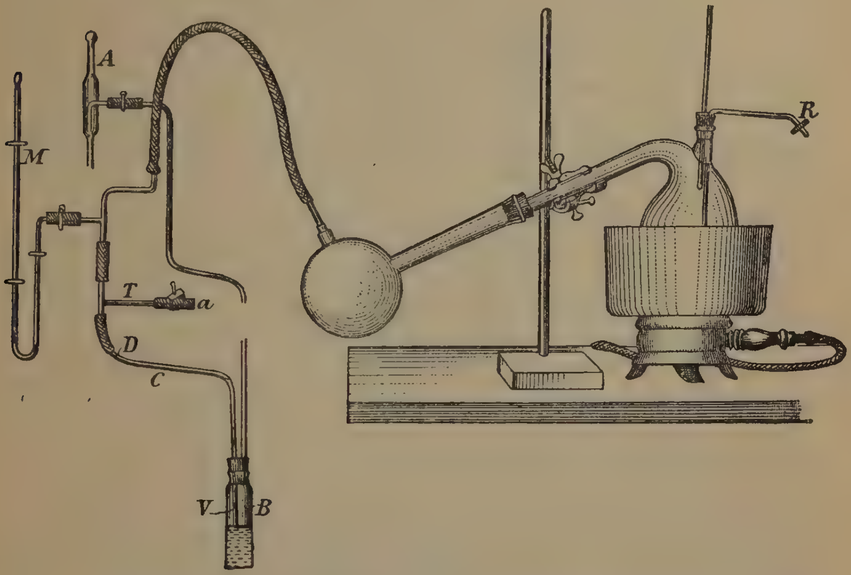

Fig. 48. Distillation under Reduced Pressure with Safety Appliances (Lassar-Cohn)

as a means of stopping the bumping of boiling liquids. Under the heading "Stirring and Shaking" a metal apparatus "provided with a stirrer" which permits distillation under reduced pressure without simultaneous passage of air, will be discussed. However, its applicability is so rare that it is scarcely worth while to consider it as a practical substitute for glass apparatus.

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[5] Anschütz, R., *Destillation unter verminderten Druck im Laboratorium,* Bonn, 1885, p. 2.

[6] Pellogio, P., *Z. anal. Ch.*, **6**, 396 (1867).

When liquids which foam badly are to be concentrated in vacuo, they are allowed to drop into the distillation flasks placed in a properly heated bath. Thus, Fischer[7] dropped a badly foaming ether solution into a distillation flask standing in water at 50°. In this connection, consult the method given under the heading "Delay in Boiling and Foaming over of Liquids." This may be used for large quantities, and has proved of value for even the most difficult cases.

If the distillation is carried out at a pressure of only 0.3 mm. of mercury, or even in the vacuum of the cathode discharge, as is now frequently done, (see the close of this division) then the Dittmar device cannot be used. It should be noted that Stock[8] has constructed an excellent apparatus, too complicated to reproduce here, that permits the most exact experimental treatment of small quantities of volatile materials in a vacuum. The material is handled in a closed apparatus, completely evacuated by a mercury air pump, excluding all temperature rises, air and other gases, fat, etc. In general, the materials come in contact with only glass and mercury. The isolation and purification are accomplished by fractional distillation; the testing of uniformity and identification, particularly by measurement of tensions at suitable temperatures. Since none of the substance is lost, a few tenths of a gram suffices for an extensive investigation, including the determination of the most important chemical properties and physical constants.

DEGREE OF VACUUM FOR DISTILLATION AND ITS REGULATION

About forty years ago, Krafft[9] still recommended working at a pressure of 100 mm. of mercury, a condition in which small variations had much less influence on the thermometer reading than at very

[7] Fischer, Emil, and Fischer, Hans, *Ber.*, **43**, 2526 (1910).

[8] Stock, Alfred, *Ber.*, **50**, 991 (1917).

[9] Krafft, F., *Ber.*, **15**, 1692 (1882).

small pressures.[10] At this pressure, bumping of boiling liquids, discussed above at length, practically never occurs, while at the lower pressure special care must be taken to avoid this. This pressure is low enough to completely protect many materials from decomposition. For this reason, it appears to the writer that a pressure of 100 mm. is used too infrequently considering the convenience it affords. It is often possible at this pressure to replace a complicated apparatus with an ordinary one made, for instance, from a Claisen flask and a retort receiver connected with an air pump, and if glass fragments are placed in the flask, it is not necessary to draw air through it.

To reduce the variations of pressure in such simple apparatus to 0.1 to 0.5 mm., Krafft interposes between it and the air pump a stout walled vessel *A* (fig. 49) which, if large enough, regulates almost perfectly the working of erratic air pumps, and also serves as a vacuum reservoir. If this vessel is connected with the atmosphere (or with a gasometer containing hydrogen or carbon dioxide) by means of the apparatus *B*, which carries two stop cocks, and if the external one has a fine opening, it is possible, after a little practice, to establish any desired pressure, provided the flow of water to the pump has been regulated[11] to approximate this pressure, which may then be maintained for hours.

Kahlbaum[12] has proposed another regulator, and in discussing this question, five years after Krafft's[13] proposal, states that the entire advantage of distillation under reduced pressure is not utilized until the pressure has been reduced to 25 mm. or less. This viewpoint is now generally accepted, perhaps erroneously. Since the water pumps now used will usually, with ease, give a vacuum of 8 mm., it has become customary to work at a pressure of from 8 to 20 mm. of mercury.

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[10] Thus at a pressure of 10 mm., a difference of 1 mm. amounts to about 10 per cent, whereas at 100 mm. it corresponds to only 1 per cent. A new factor comes into consideration at the low pressure, namely the pressure necessary to overcome the frictional resistance to the passage of the vapor through the side-arm; this varies with the velocity of the vapor, so that, even when distilling under the relatively high (6 to 20 mm.) pressures of the water-pump, the indicated boiling point of a liquid may be raised several degrees by increasing the rate of distillation. For this reason, it is advisable to distil as slowly as possible when it is desired to observe the boiling point at the working pressure.—H. T. C.

[11] This is a very dangerous practice, and is not to be recommended. The pressure should be regulated by means of a screw-clamp on the thick-walled india rubber tube connecting the pump to the apparatus. If the water-valve be throttled down, any diminution in the pressure in the water-main will cause water to be sucked from the pump into the apparatus, with possibly disastrous results.—H. T. C.

[12] Kahlbaum, G. W. A., *Ber.*, **27**, 1386 (1894); see also Schall, C., and Paschkowetzky, *Ber.*, **25**, 2885 (1892).

Krafft,[14] in 1895, made astounding advances and showed that the results obtainable in real vacua were far in advance of those possible at even very low pressures. His first triumph, by the new method, was the preparation of crystalline lactic acid[15] which had been the goal of more than a century's fruitless effort. If lactic acid is distilled, as long as a measurable pressure is present in the apparatus, it either retains some water, or partially loses water, going over to the lactide or lactic acid anhydride, and the real acid will then no longer crystallize. At the vacuum reached by him, as he soon found, the cathode glow suddenly appears, and therefore, this method is known as distillation in the vacuum of the cathode glow.

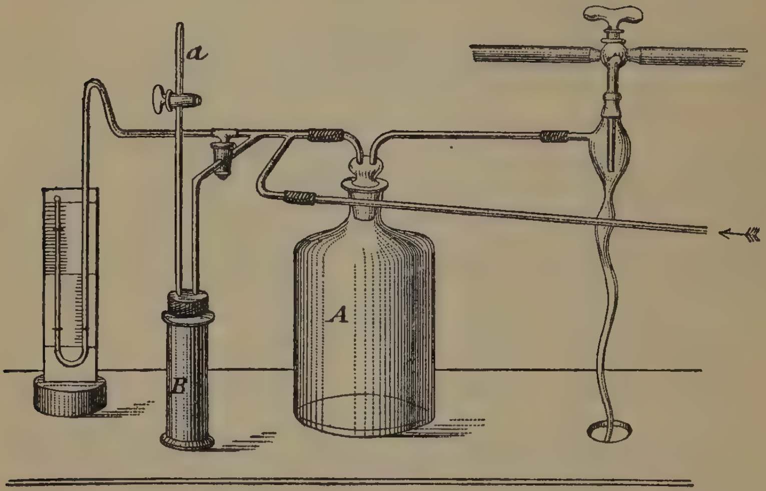

FIG. 49. PRESSURE REGULATOR FOR VACUUM DISTILLATION (KRAFFT)

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[13] Krafft, F., *Ber.*, **15**, 1693 (1882); *Ber.*, **27**, 1823 (1894).
[14] Krafft, F., and Weilandt, H., *Ber.*, **29**, 1316 (1896).
[15] Krafft, F., and Dÿes, W. A., *Ber.*, **28**, 2591 (1895).

The development of distillation under reduced pressure has been such that the two species must be kept separated, namely, the one in which 8 to 20 mm. of mercury pressure is used, and the second in which the vacuum of the cathode glow or, at most, a pressure of not more than about 0.25 mm. mercury is maintained. The former is easily carried out wherever a water system allows the use of a water air pump; the latter, however, requires much more delicate apparatus and considerable skill on the part of the experimenter. In general, laboratories attempt to get along with good water pumps. The recent advances in high vacuum methods for chemical purposes are extraordinary, and Gaede has made practicable entirely new methods of producing high vacua. A number of other investigators have successfully followed his lead.[16] After the points common to both procedures have been discussed, each one will be treated separately.

VACUUM CONDENSERS

Vacuum distillations may usually be made without condensers. If one is used it suffers usually from the disadvantage that the vapors of the distillate are easily drawn through the vacuum pump and lost. Gödecker has devised a vacuum condenser (fig. 50) for combating this evil, which has the following additional merits: (1) The vapors cannot reach the vacuum pump since the exhaustion tube *C* is not directly connected with the cooling tube, but with the receiver in which the residual vapors are cooled; (2) The vapors have a greater resistance because they impinge against the walls of the new condenser and the receiver which are properly cooled. When in use, the projection *C* of the condenser is connected with a water air pump. The receiver, which may also be cooled, is fastened by means of a rubber stopper, and is evacuated through the tube *C* and the two openings *D*. The arms *A* and *B* provide for the entrance and exit of the cooling water. The condenser may also be used directly for refluxing.

AIR PUMPS

Any ordinary water pump will satisfactorily evacuate apparatus, if a vacuum of 6 to 20 mm. is sufficient. Fischer and Harries used a two stage Geryk vacuum pump to obtain a pressure of only 0.15 mm. of mercury. Figure 51 shows such a pump electrically driven which may be used either for the attainment of high vacua, or if reversed, as a pressure pump. Figure 52 shows a Wohl vacuum meter.

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[16] Gehrts, F., Comprehensive information on this may be found in *Naturwissenschaften,* 7, 983 (1919); see also Volmer, M., *Z. angew. Ch.*, **34**, 149 (1921).

The molecular air pump of Gaede,[17] starting with a pressure of 6 mm. will produce hard Roentgen rays in six seconds. This required more than half a day before the invention of this pump.

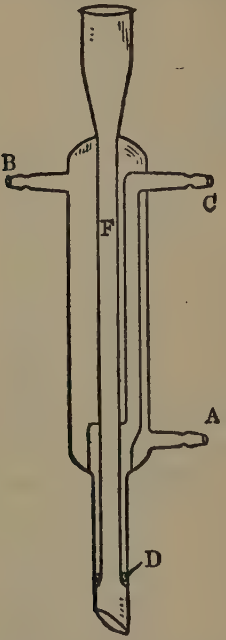

FIG. 50. GÖDECKER VACUUM CONDENSER

A recent mercury air pump will be described in detail, because such pumps require no special driving motors, available in but few laboratories. Mercury vapor pumps will be discussed later.

According to Beutell,[18] a practical mercury air pump designed for high vacua must fulfil the following requirements: (1) it must be easily handled and work with certainty, even without supervision;

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[17] Gaede, W., *Physik. Zeit.*, **14**, 1238 (1913).

[18] Beutell, A., *Ch. Zt.*, **34**, 1342 (1910).

(2) it must quickly produce the highest vacua; (3) it must withstand the impacts of the mercury in vacuum; (4) the quantity of mercury must be as small as possible, because of its expense; (5) the mercury should not pass through cocks or rubber tubes, since it is impossible to attain a high vacuum with dirty mercury; (6) the pump must be quickly and easily cleaned. After years of effort, Beutell succeeded in constructing a simple pump fulfilling these six requirements. Although shorter, it works just as rapidly as the Kahlbaum pump,[19] and is also more rapid and better than the pumps of Geisler and of Töpler. Only motor driven mercury pumps, like Gaede's, which will be considered presently, exceed it in speed, but their motive power is a constant expense. Figure 53 represents an intermediate type, but the cathode tube accompanying every pump to serve for orientation in high vacua, is not shown. The mercury is poured into the beaker-like vessel at the lower right, and this is closed by a fitted ground glass stopper. After the tube at the upper right is exhausted by a water pump, the rest of the mercury in the beaker is allowed to enter the pump, by raising the lower ground stopper, but care must be taken that some mercury remains to seal the ground joint. The cock in the same ground stopper is now opened by turn-

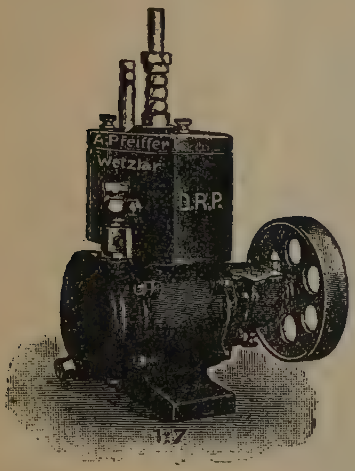

FIG. 51

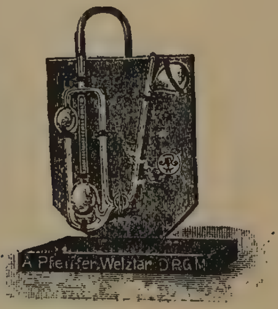

FIG. 52

[19] Kahlbaum, G. W. A., *Ann. Phys.*, **6**, 591 (1901).

ing it 180 degrees, so that the air necessary to raise the mercury may enter through the asbestos plug within. The regulation of the current of air need not be made each time by means of the cock, but may be done by the carefully tested asbestos plug. The pump will continue to work for days and weeks without supervision, and the same small quantity of mercury will circulate continuously in the two vertical tubes. The mercury remains perfectly clean because it touches nothing but glass, and furthermore, the entering air is filtered. It is well to protect the asbestos against particles of fat and dust by a pad of cotton-wool. The pump is stopped by turning

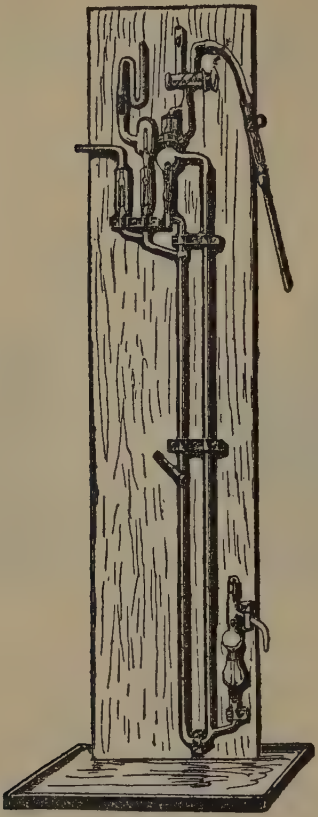

Fig. 53. Automatic Rapid Mercury Pump for Highest Vacuum (Beutell)

first the lower and then the upper cock through 180 degrees, whereupon the pump slowly fills with air. The asbestos plug in the two-way cock makes it impossible for the air to enter too quickly, thus removing the danger of the pump being shattered in this way. In spite of the short fall tube, the pump works very rapidly because of the knee shaped drop former at the top, and this imparts a strong electric charge to the mercury by friction on the glass walls. This alone makes it possible to make a cut-off in the upper part, even though wider fall tubes are used. The danger of breaking the fall tube by the impacts of the falling mercury combined with violent electrical discharges, is not present in this pump, because air is constantly entering through the small slanting tube at the left of the fall tube. This tube is closed with a well fitted cork so as to admit only very small quantities of air. The air diffusing through its pores is sufficient to form a constantly renewed air cushion which softens the violent blows of the falling mercury. At the same time, the dangerous spark discharges disappear, and in their place, there is the glow of the ordinary Geisler tubes. Beutell has run one of these pumps continuously for fourteen days at the highest vacuum without damage to it; and during years of experience with pumps of his design, a fall tube has never broken. Not much is demanded of the water pump. When this is acting under a pressure of 6 to 8 cm. of mercury, the level in the fall tube drops below the cork admitting air. This is essential or it would be thrown out of action. Because of the small volumes of the pumps themselves and the correspondingly small quantities of mercury required, which in the three types available, lie between 8 and 20 cc., it is possible, by using clamped off accessory apparatus, to produce a Roentgen vacuum in fifteen seconds with type 1, and in one minute with type 3. The auxiliary cathode tube exhibits intensive cathode and Roentgen rays in one or two minutes with types 1 and 3, respectively. In order to clamp off the accessory apparatus, including the drying train, at any desired vacuum, or to be able to interrupt the pump at any time, these pumps may be ordered with a cock. After working for days, a yellowish gray coating of yellow mercuric oxide mixed with metallic mercury appears in the ascending tube, but the circulating mercury remains perfectly clean and bright. The pumps may be removed from the support with a clamp when they are to be cleaned. This cleansing is best done by hot aqua regia, followed by rinsings with clean water. Nitric acid alone is not recommended because the mercury nitrate produces a white precipitate with water. The ground-in tip out of which the mercury flows is removed first and is best cleaned by carefully heating it over a gas flame. It is especially important that only pure mercury be used in these pumps, otherwise it oxidizes rapidly and fails at high vacua. It should be remembered that when mercury is purified by vacuum distillation, that not only fat and its decomposition products, but also dissolved metals, like zinc, lead, etc., also pass over quantitatively under the reduced pressure. For many years Beutell has used the following very simple method of cleaning mercury: all dirty mercury is stored in a flask along with some concentrated sulfuric acid until a sufficient quantity has accumulated. This is then washed with water under the tap, and then boiled with a strong solution of sodium hydroxide. After repeated washing with water, the mercury is dried with filter paper and poured, while still hot, through a filter whose stem has been cut off. It remains perfectly bright and is suitable for pumps, manometers, and similar apparatus.

Type 1 and 2 are particularly adapted for rapid working in technical and scientific institutions, while type 3 is designed for laboratory use where speed is not so important.

Attention should be called to Friedrich's mercury vapor pump. It is not affected by steam or acid vapors, requires no drying agents, produces the highest vacuum in a very short time, is easily cleaned and is certain in action. The range of this pump is 15 to 0.000006 mm. with ordinary stop cocks, and so permits the use of a water pump for producing preliminary vacuum. The pump works in such a way that it is not affected by water, acid, or any other vapors, in so far as they do not markedly attack mercury and glass. It is, therefore, especially suited for high vacuum distillations, drying, determinations of tensions, etc.

Dewar's[20] method of rapidly obtaining high vacua is given here because it may occasionally be very useful. Freshly heated charcoal absorbs and retains gases. This property is enhanced many times if the charcoal is kept at a low temperature, and then becomes so considerable that it can evacuate a closed space within a short time. It is only necessary to provide the vessel with a side tube containing the best quality of cocoanut charcoal, and then dip this tube into liquid air. Within a few minutes a vacuum sufficient for the production of cathode and Roentgen rays is obtained. Wohl[21] has described an apparatus built on this principle, suitable for chemical laboratories, and has given an extensive bibliography. He uses blood charcoal. Erdmann[22] uses cocoanut charcoal. Other methods of completely evacuating a distilling system in which the apparatus must be previously filled with carbon dioxide will be discussed later.[23]

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[20] Dewar, J., *C. R.*, **139**, 261 (1904).

EXCLUSION OF MOISTURE FROM THE DISTILLATION SYSTEM

If the moisture entering the apparatus from the water pump is a disturbing factor, a tube filled with phosphoric anhydride should be put between the two. On the other hand it is not absolutely necessary to treat high boiling oils with drying agents, such as calcium chloride, as is done in ordinary distillations to avoid bumping, though it is advisable to do so. They may be directly distilled in vacuo because the water passes over first. Knoevenagel[24] found that if crude methylene dimalonic ester is kept for a long time in the distilling apparatus, at 50° and 12 mm. pressure, all the water disappears, and the ester itself then distils quietly between 190 to 200°.

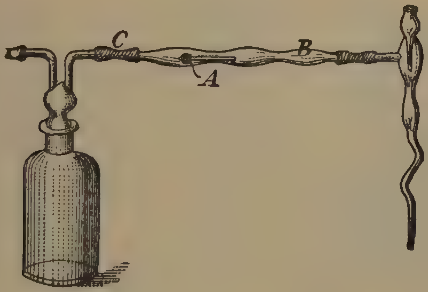

Fig. 54. Back Pressure Valve

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[21] Wohl, A., and Losanitsch, M. S., *Ber.*, **38**, 4149 (1905).

[22] Erdmann, E., *Ber.*, **39**, 192 (1906); Wohl, A., *Ber.*, **39**, 513 (1906).

[23] Extremely active charcoals have been developed for use in gas masks. —E. E. R.

[24] Knoevenagel, E., *Ber.*, **27**, 2346 (1894).

SAFETY DEVICES

Evacuated apparatus seldom breaks but, nevertheless, it is advisable, during such distillations, to wear goggles, or still better, a mask to avoid possible injuries from flying particles.

Since the ordinary water pumps are usually used, beginners especially, may suddenly shut off the water at the end of a vacuum distillation, whereupon, the water sucks back into the distillate. So it is best to place a large empty flask between the receiver and the pump to catch this water, or to insert a back pressure valve, or even take both precautions. This valve (fig. 54) consists of a somewhat pointed glass rod *A*, with a piece of rubber tubing drawn over the pointed end. It lies free in the tube *B*. If the water comes back from the pump, it carries the glass rod with it, which then catches in a constriction in the tube *C* and keeps the water from going any further.

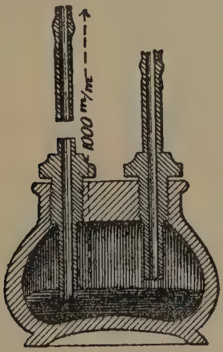

Fig. 55. Iron Mercury Container Used as Safety Measure in Low Pressure Distillations (Lassar-Cohn)

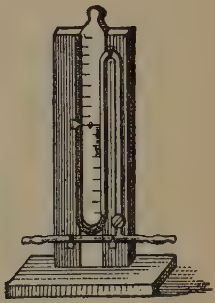

Fig. 56. Manometer

This device which is not absolutely reliable, is replaced in the Königsberg laboratory by another one, seemingly more complicated, but absolutely dependable. Any one can make this very easily, and twenty years' of experience with it have proved its value. It is shown in figure 48, and consists of the following: a tube goes from the air pump *A* through a stopper into the neck of the flask *B* which contains mercury. Through the second opening of the stopper, passes a tube *C*, leading to the distillation apparatus and dipping under the mercury. Consequently the air drawn from the apparatus by the air pump must pass through this mercury. The length of this second tube to the point *D* is about 800 mm. The apparatus to be evacuated is connected with it by inserting a T tube. If the pump suddenly ceases to work, the mercury will rise about 760 mm. in the tube *C*. But since this is 800 mm. long up to *D*, none of the mercury will get into the evacuated distillation flask, whose contents will never then be endangered through any irregular working of the air pump. A piece of rubber tubing, *a*, leading to the open air is fastened to the T-tube and is closed, during the distillation, by a screw clamp. When the distillation is finished, a slow current of air may be admitted to the evacuated apparatus by opening the clamp. The other branch of the tube *C* leads to the manometer *M*. Kähler and Martini of Berlin have improved the device by making of iron, both the mercury vessel which rests on its base, and the tubes leading to it (see fig. 55). The use of the iron apparatus is otherwise no different, except that the parts resting on the bottom are thus made unbreakable. The pinch clamp *R* regulates the admission of the air bubbled through the liquid in order to prevent the bumping of the distilling liquid, and the constriction of the glass tube at *V* keeps the mercury from rising too rapidly when the air pump is turned off.[25]

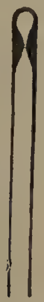

FIG. 57. MERCURY MANOMETER WITH CONSTRICTED HEAD (LASSAR-COHN)

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[25] An extremely simple and reliable check valve, prepared from two india rubber stoppers and three pieces of glass tubing, has been described by Brewster (*Ind. Eng. Chem.*, **15**, 32 (1923)).—H. T. C.

MANOMETERS (VACUUM METERS)

A very sensitive manometer will be discussed later in connection with the Gaede pump. The manometers ordinarily used are nothing but shortened mercury barometers. Figure 56 shows a portable form of these such as is commonly used in vacuum distillations. The scale on the mirror allows a rather exact reading of the pressure existing in the apparatus during the distillations.

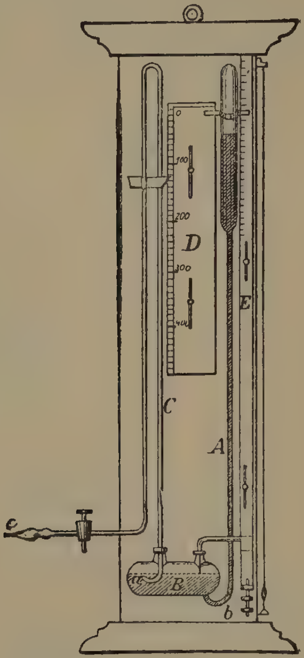

Fig. 58. Manometer for Exact Pressure Readings (Vis)

Vis[26] was the first to point out that these U-shaped manometers have the disadvantage of soon becoming inaccurate in case the mercury is allowed to strike back rapidly several times in the closed arm; the experience of many before him. As is well known, this often causes the head of the closed end to break off since it cannot withstand the impact of the mercury. For many years, the writer definitely prevented this by greatly thickening the tubes of his manometer just below their closed ends. The rising mercury must now force its way through this narrow passage, and its impetus is so reduced that the apparatus never breaks (fig. 57).[27]

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[26] Vis, G. N., *Ch. Zt.*, **24**, 37 (1900).

According to Vis, air is always carried along, if the mercury rebounds rapidly, and this produces a permanent error. Since great accuracy is never expected of metal vacuum meters, he has constructed the following type free from this disadvantage and which has given him good service. It may replace the barometer in the laboratory (see fig. 58).

The vessel *B* of the syphon barometer *A* is larger than usual. The tube *C* connected with the system to be evacuated, dips into *B* and is drawn out at the end *a*. It is bent in a direction opposite to that of the barometer tube, but, of course, so that the opening at *a* is still below the mercury. This bend, like the one at *b* on the barometer tube, serves to keep any air carried along when the vacuum is released, out of the barometer vacuum. At the other end of *C* is a three-way cock through which the end tube *c* may be connected with the tube *C* and also with the atmosphere. A movable pointer is attached to the tube *C*. Between the tubes *A* and *C*, is a scale divided into millimeters which may be moved so that the pointer may be placed at the zero, indicating the height of the barometer. Next to *A* is another scale also divided into millimeters and this may be moved by set screws so that the zero point coincides with the lower mercury level in *B*. The zero point is determined by an index as is usual in reading barometers. The difference between the prevailing vacuum and the absolute one is measured on the scale *D*, placed between *C* and *A*, by means of the movable pointer fastened to *C*. A plummet hangs on the side. The apparatus is mounted on wood and may be hung on the wall.

Ubbelohde[28] states that it is very difficult accurately to measure pressures prevailing during vacuum distillations, even though the very sensitive MacLeod vacuum gauges are used, because the mixture of traces of air and of saturated vapors is not the same at the gauge and in the receiver.

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[27] A modification of this manometer, in which it is impossible for air to find its way into the closed portion of the tube, is described in *J. Amer. Chem. Soc.*, **42**, 786 (1920).—H. T. C.

[28] Ubbelohde, L., *Z. angew. Ch.*, **21**, 1454 (1908).

DISTILLING FLASKS FOR VACUUM DISTILLATIONS

The regular use of vacuum distillation, with its many advantages, is greatly facilitated, if a number of distilling flasks of varying capacities, but with necks and exit tubes of the same length and width, are available. The same sized glass tubing should be used for making the capillaries, so that the same stoppers may be interchanged.

It is necessary to bubble a current of air or indifferent gas through the distilling liquid, if the distillation at low pressure is to be quiet. This method is not satisfactory in some cases. The final solution of this problem is given under the heading "Delay in Boiling and Foaming Over of Liquids." Figure 48 shows how air may be bubbled through an ordinary retort or a flask. A thermometer is passed through one opening of a double bored stopper and through the second a glass tube whose lower end within the retort has been drawn out to a capillary. Anschütz has sealed the capillary right into the flask (fig. 59), or if a thermometer is not necessary, he recommends that the capillary be fastened in the drawn out neck of the flask by means of rubber tubing. The simplicity of this last arrangement has much in its favor.

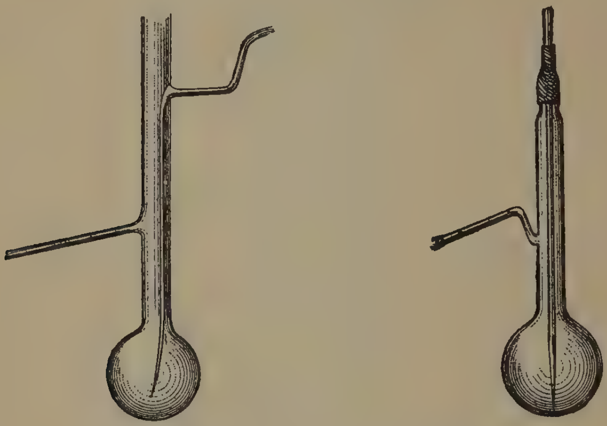

FIG. 59. DISTILLING FLASKS (ANSCHÜTZ)

With reference to reducing the leakage in such apparatus, it may be mentioned that it was long customary, when assembling it, to use, if possible, no cork, but only rubber stoppers. Then Brühl[29] showed that thick collodion solution is excellent for making cork seals tight. This glazes the corks and makes them absolutely air tight. Consequently, this is worthy of consideration, and is of particular interest to laboratories where rubber stoppers of all sizes are not available. He reconsidered this point later,[30] and stated that he then always used rubber stoppers for vacuum distillation, insuring that they are not attacked at high temperatures more than cork ones, by placing them at such distances that the hot vapors hardly reach them.[31]

Hell and Jordanoff[32] recommend that the tube drawn out to a capillary be held by a special clamp, if a rubber stopper is used, because it often happens that the rubber softens during the distillation following excessive and sometimes unavoidable exposure to the hot vapors. The stopper then is drawn into the retort, the capillary breaks off, and the distillation which is proceeding nicely, is interrupted. The Anschütz flasks with sealed-in capillaries have the disadvantage that the capillary can only be cleaned with difficulty, if at all, in case the distillation residue becomes very viscous. Using the same principle as Anschütz, Lederer[33] has avoided this by slightly modifying the ordinary fractionating flask. He has inserted between the real body of the flask and the neck, a cylindrical projection (see fig. 60) and a glass tube drawn out at both ends to a fine capillary, is fastened in this by a stopper. Because of its flexibility, the end of the capillary in the boiling space may easily be moved into the deepest part of the flask by properly adjusting the stopper, so that the capillary functions to the very end of the distillation.

Claisen distilling flasks,[34] now the most commonly used, have double necks (fig. 61). One of these serves for the capillary tube, while the other takes the thermometer. The upper openings are of such size that a piece of rubber tubing may easily be slipped over them, and still allow the capillary tube and the thermometer to pass through easily. The necks may, of course, be made large enough to accommodate one hole stoppers. This avoids the disadvantages attending the use of two hole rubber stoppers, namely, the frequent breaking of the capillary, and the crushing of the thermometer. Furthermore, it is of particular importance that it is much less likely that any liquid will be thrown into the condenser by bumping, than when a single necked flask is used. This can almost certainly be avoided if the side tube, which now may not be constricted, is filled with pieces of glass large enough not to fall into the flask. These will break the impact of any liquid which may be thrown upward.

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[29] Brühl, J. W., *Ber.*, **24**, 3375 (1891).

[30] Brühl, J., *Ber.*, **26**, 2510 (1893).

[31] Cork stoppers are preferable in vacuum distillation as they are not attacked by vapors of organic substances and do not soften.—E. E. R.

[32] Hell, Carl, and Jordanoff, Christo, *Ber.*, **24**, 937 (1891).

[33] Lederer, L., *Ch. Zt.*, **19**, 751 (1895).

[34] Claisen, L., *Ann.*, **277**, 177 (1893).

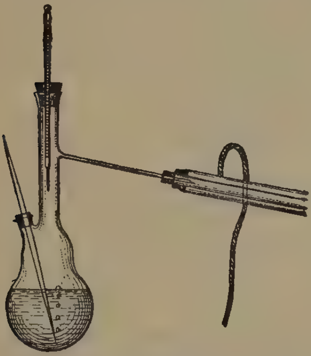

Fig. 60. Distilling Flask (Lederer)

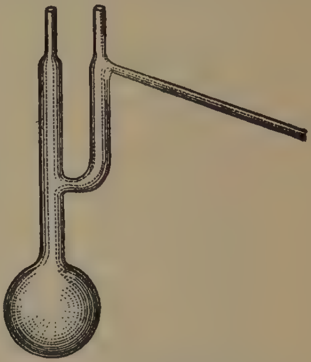

Fig. 61. Distilling Flask (Claisen)

This end is more surely accomplished by following a proposal of Angeli.[35] He found that, in spite of all precautions, the overheating of small quantities of liquids often occurs, causing a part of it to be thrown into the receiver. He avoided this by almost completely filling the distillation flask with glass wool, and after this had soaked up the liquid, he distilled from a bath. Claisen further recommends that the space above the coarse fragments of glass be wholly or partially filled with glass beads, and so combine the advantages of the Hempel column with vacuum distillation. Obviously, this may only be done with liquids whose boiling points are not too high. He accomplished more rapid separations and obtained much sharper boiling points by this method, than by the ordinary one. Even though fragments of glass and beads are not used, as a consequence of the long path traversed by the vapors, there is not the same difference between heating over a free flame and distilling from a bath, as the writer always recommends, as is apparent when a flask with a plain neck is used.

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[35] Angeli, A., *Gazetta*, **23**, II, 104 (1893).

RECEIVERS FOR VACUUM DISTILLATIONS

Ordinary receivers may usually be employed in the distillation of liquids in vacuo, as shown in figure 48. If the condensate solidifies rapidly, the condenser may clog, since it cannot be externally heated at the places where there are rubber connections. Receivers of sufficient capacity, directly sealed to the flask, are used in such cases. Anything solidifying in them may be melted, even during the distillation, by heating. The first of the forms shown (fig. 62), as well as the idea itself, is due to Anschütz, the second to Muencke. These short projections often suffice, during vacuum distillations, as condensers, especially if they are placed in ice water, or if water is allowed to flow over them after they have been enveloped in bibulous paper. If this device is not satisfactory, a longer glass tube, serving as an air condenser will practically always answer the purpose. Actual water condensers as shown in figures 60, 64, and 72 are only seldom necessary.[36]

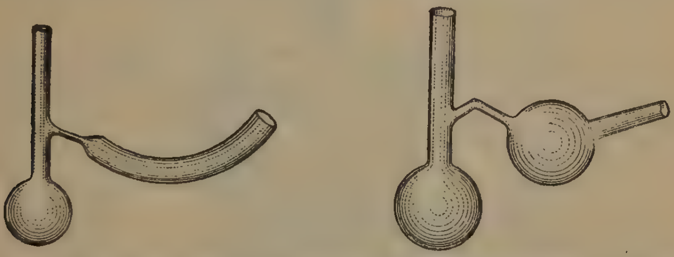

FIG. 62. DISTILLATION FLASKS WITH FUSED ON RECEIVERS (ANSCHÜTZ)

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[36] Such a tube should be quite wide, say 10 mm. internal diameter for a flask of 500 cc. capacity, so that the first runnings, which are apt to solidify on entering the cold parts of the tube, do not clog the tube before the further supply of hot vapor and condensate melts the solid which forms at the outset. Indeed, the use of unconventionally wide and long side-tubes, which are employed in conjunction with a cooled receiver without interposition of a jacketed condenser, has much to recommend it.—H. T. C.

FRACTIONAL DISTILLATIONS UNDER REDUCED PRESSURE

Numerous types of apparatus have been devised for changing the receivers during vacuum distillations, without necessitating an interruption of the distillation. A large number of these devices, one or an other of which will certainly serve the purpose, are reproduced here. In case the receivers must be removed this must be done without losing the vacuum in the distillation system. It must be possible to admit air into the receiver, since otherwise, it cannot be loosened because of the external air pressure. Consequently, three way stop cocks must be used in such apparatus as soon as larger quantities of liquids are dealt with, while Brühl[37] has sought to avoid them in his apparatus for smaller quantities. This was based on a principle first used by Konowalow[38] (fig. 63). The glass cylinder *A* may be evacuated at *a;* it has an opening on one side, and is closed by a ground on cover. The condensing tube *c* passes through a rubber stopper inserted into the side tube of the cylinder *A*. A glass rod *e*, provided with a handle, passes through the center opening *d* of the cover, and this also is made tight by a rubber stopper. The

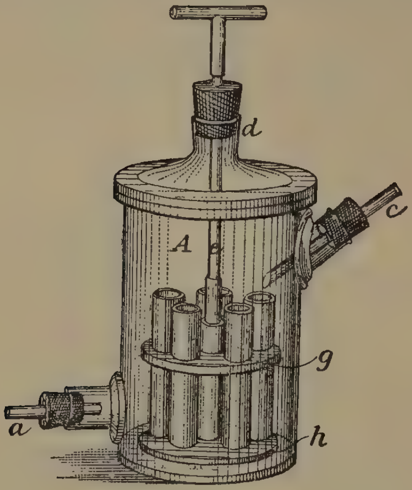

FIG. 63. RECEIVER FOR VACUUM FRACTIONAL DISTILLATION (BRÜHL)

glass rod extends almost to the bottom of the cylinder *A* and has a hole bored through it, some distance from the lower end. A pin goes through this hole on which the receptacle holder can be hung by means of a bayonet catch. The holder consists of a collar on which the disks, *g* and *h*, are fastened. The test tubes which serve as receivers are set into the circular holes of the disks. This arrangement permits the frame to be rotated after the cylinder *A* has been evacuated, and the distillate may be fractionally collected in the individual receivers, without having to open any part of the apparatus. The cover and cylinder may be sealed by means of the grease mixtures recommended in this volume.

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[37] Brühl, J. W., *Ber.*, **21**, 3339 (1888); *Ber.*, **26**, 2510 (1893).

[38] Konowalow, D., *Ber.*, **17**, 1535 (1884).

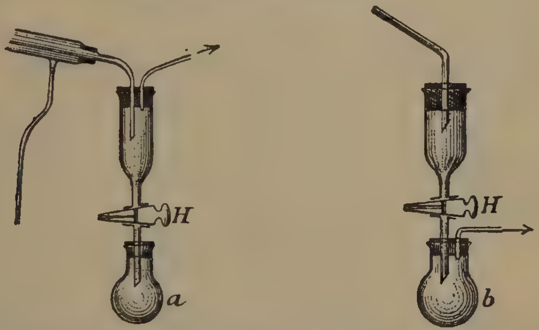

Fig. 64. Receivers for Vacuum Fractional Distillation (Lederer)

Figure 64 shows two receivers devised by Lederer.[39] In the form *a* the distillate coming from a condenser runs into a cup, through whose double bored stopper a second tube runs to the air pump. The three-way cock *H* also allows the small flask serving as receiver, to be connected with the distillation apparatus in such a way that it may also be evacuated. To remove it after a fraction has passed over at a definite boiling point, the three-way cock is turned so that the vacuum is maintained in the distilling apparatus by the pump, but air may enter the small receiving flask. It may then be removed, replaced by another, and the fractionation continued after the cock has been turned again.

Figure 64 *b* shows how the proper setting of the three-way cock *H*, permits the air pump to be cut off during the removal of the receiving flask. After this has been replaced by another, the new receiver may be evacuated before it is connected with the distillation apparatus. This is not possible in the arrangement shown in figure 64*a*. However, the small quantity of air in the flask will be so rapidly removed by a good water pump, after opening the three-way cock, that it is of little significance.

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[39] Lederer, L., *Ch. Zt.*, **19**, 751 (1895).

Fogetti[40] described the apparatus shown in figure 65 for the fractional collection of distillates obtained in vacuo, after he had thoroughly tested it for three years. Like the Brühl apparatus, it avoids the necessity of interrupting the distillation each time the receiver is changed. It consists of three separatory funnels which have been sealed into each other. Each of the three bulbs has, at the same height, a side tube carrying a glass cock, and the upper bulb, for practical purposes, has two such side tubes. The apparatus is used as follows: the cock *c* is connected with the pump. The first fraction is caught in the bulb *A*, cocks *d*, *e*, and *f* being closed, and cocks *a*, *b*, and *c* being open. When changing the fraction, cock *a* is closed, and the bulb *A* is emptied. The second fraction collects

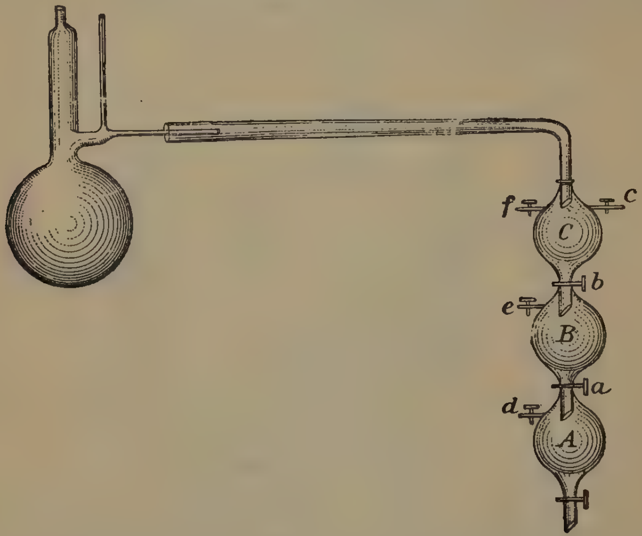

FIG. 65. APPARATUS FOR VACUUM FRACTIONAL DISTILLATION (FOGETTI)

in bulb *B*. When it is changed, the cock *b* is closed and the bulb *B* emptied. While the third fraction is collecting in bulb *C*, bulbs *A* and *B* are evacuated by a separate pump, until the same pressure prevails as in bulb *C*. To catch the fourth fraction, the contents of bulb *C*, are transferred to bulb *A*, by opening cocks *a* and *b*, and *a* is then closed. While the fourth fraction is being collected in bulb *B*, bulb *A* is emptied and so on. This apparatus may be improvised by connecting separatory funnels, using double bored rubber stoppers and bent glass tubes provided with pinch clamps.

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[40] Fogetti, Lucien, *Ch. Zt.*, **24**, 374 (1900).

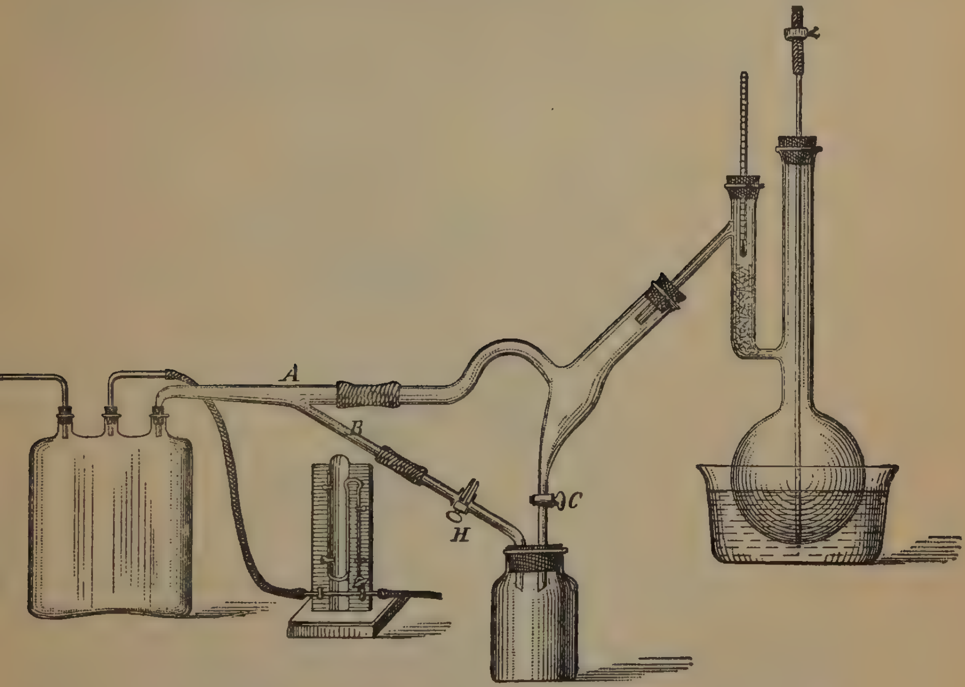

FIG. 66. ENLARGED APPARATUS FOR FRACTIONAL DISTILLATION UNDER REDUCED PRESSURE (THORNE)

Figure 66 reproduces another complete, somewhat larger apparatus, designed for distillation under reduced pressure. This may be made with the aid of a few glass cocks. The principle of this is due to Thorne,[41] and the writer used this arrangement for a long time, with satisfactory results. The outer neck of a Claisen flask is filled with glass fragments, and the thermometer placed above them. A metal bath containing Wood's metal, as recommended by Krafft,[42] is used for the distillation. The distillate passes directly into a kind of adapter, since condensers are but seldom necessary. The adapter is connected at one side with the receiver through the cock *C*, and on the other side, with the vacuum reservoir, the air pump, and the manometer, by the tube *A*, which is so arched that the distillate cannot run into these parts. The vacuum reservoir is a vessel of about 3 liters capacity with three openings. A tube *B* leads from the two-hole stopper of the receiver to the tube *A*. The tube *B* may be closed by a three-way cock *H*. This permits changing the receiver, without losing the vacuum in the distillation flask, and connects it with the outer air so that it may be taken off. The distillate coming over while the receiver is being changed is collected during the short time this requires, above the cock *c*, and runs into the new receiver after the vacuum has been established in it. The apparatus

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[41] Thorne, L. T., *Ber.*, **16**, 1327 (1883).

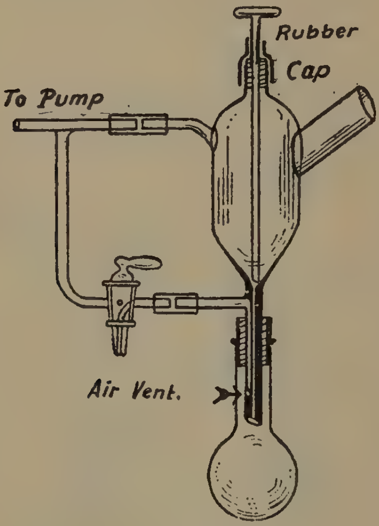

FIG. 67. FRACTIONATING APPARATUS (KOLBE)

is made more flexible by cutting the tubes *A* and *B*, and reconnecting them with rubber tubing. It is obvious that Brühl's revolving receiver may be used in place of the receiver shown in the figure.

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[42] Krafft, F., and Dÿes, W. A., *Ber.*, **28**, 2588 (1895).

Kolbe[43] believes that it is important to avoid apparatus designed for fractional distillation in vacuo, that has the adapter and receiver separated by a cock. In many cases, the use of a lubricant is decidedly out of the question. He says that the friction valve is much better than a cock, since it has the advantage of being tight and never sticking. In his apparatus (fig. 67) this valve is not a fragile glass tube but a glass rod. His arrangement of the outlet leading to the pump makes it difficult for traces of the distillate to be carried very far upward. He avoids variation in pressure by pre-evacuating the receiver by a second air pump,[44] attaching the tube to the tail end of the cock, and drawing off the air through the opening on the exit tube of the adapter, below the cork of the receiver. The cock serves to admit air while changing the receiver. He recommends making the corks of vacuum apparatus tight by caps of sheet rubber which are pushed over the ends of the tubes before putting on the corks.

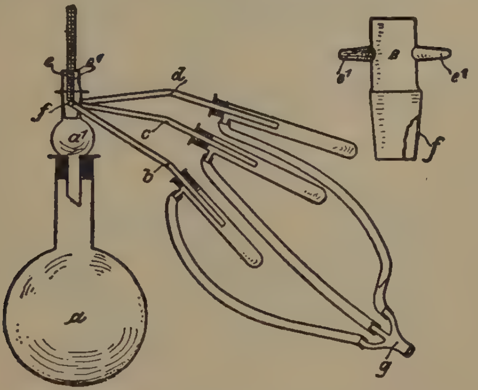

FIG. 68. FRACTIONATING APPARATUS (HAHN)

Hahn's[45] apparatus differs from the older types in principle, since the condensed distillate is not collected in separate portions, but the separation is accomplished while the liquids are still in the vapor state. This principle is applied by using distilling flasks having not one, but several distilling tubes, which may be closed in turn. His apparatus is a substitute for the neck of such a flask (fig. 68). The bulb like portion, a^1 which carries the three condensing tubes *b*, *c*, and *d* may be fastened, with the aid of a stopper, into any flask, converting it into the type under discussion. The successive closing of the tubes *b*, *c*, and *d* (there may be more if necessary) is accomplished by the revolving insert, *e*, which is provided with a side opening, *f*. The rising vapors pass through this and enter the condensing tube to which the opening *f* is adjusted. The insert, *e* is opened on top to permit the introduction of a thermometer. e^1, e^1 are pieces of glass sealed-on to serve as handles when turning the insert. The three receivers on the condensing tubes are connected with the forked tube *g* by short lengths of rubber tubing; and a tube common to all leads from *g* to the vacuum. When a fraction has passed over, the receiver filled with it is thrown out of action, first, by cutting it off from the flask containing the distilling liquids by turning the insert *f*, and, secondly, by separating it from the vacuum by drawing up a screw clamp on the tubing between the receiver and *g*. Consequently, it is not necessary to cool all the receivers at one time, and it suffices to place the one being used in ice or flowing water.

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[43] Kolbe, Gustav, *Ch. Zt.*, **32**, 487 (1908); *Ber.*, **20**, 1833 (1887).

[44] Kraus, R., *Ch. Zt.*, **26**, 1129 (1902).

[45] Hahn, Arnold, *Ber.*, **43**, 1725 (1910).

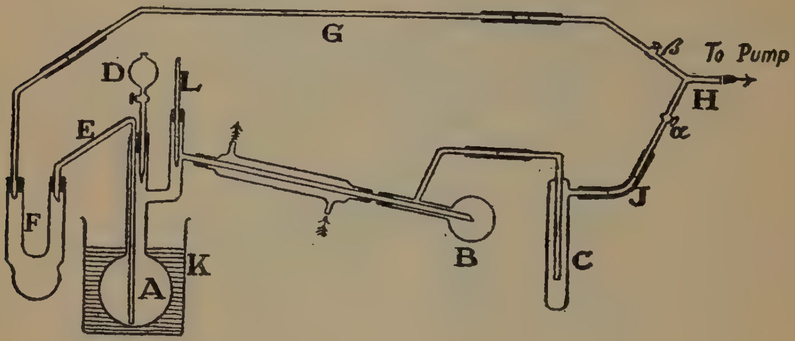

Fig. 69. Apparatus for the Removal of Residue from the Distillation Flask without Interruption of Vacuum (Bloch)

If it is necessary to vacuum distil only a part of the material in the distilling flask, and if it appears that the distillation residue decomposes new quantities of the original material so that the residue must be removed each time, then the apparatus of Bloch[46] may be used, in which the vacuum need not be broken each time.

The flask *A* (fig. 69) of about 300 cc. capacity is connected with a fractionating flask *B*, about 150 cc., through a condenser if necessary. The vessel *C* is connected with *B* and is cooled with liquid air if need be. *A* is also joined by means of the tube *E* extending to its bottom, with the U-tube *F*, whose bottom is enlarged. The forked tube *H* leads to the pump through a soda lime or calcium chloride tube and the manometer. By properly turning the glass cocks α and β, *H* may be connected either with the vessel *C* through the tubing *J* or with the U-tube *F*, through the tube *G*. The flask *A* is fed by a dropping funnel *D* whose end is drawn out to a capillary. In case the distillate is sensitive to alkali, hydrochloric acid gas is led through the whole apparatus for about ten minutes. The bath *K* surrounding *A* is then heated and the system evacuated by the water pump (α open, β closed). With the cocks in this position, in case evolution of gas is expected, 15 cc. only of the raw material is run in slowly from *D*. In such cases, a vigorous foaming occurs soon after the material begins to enter, and if more than 15 cc. is added, there is danger of foaming over. The temperature of the vapors is read on the thermometer *L*. If the distillation stops, α is closed, and β opened. The vacuum now acts through the tube *G*, vessel *F*, and tube *E*, and almost all the distillation residue is drawn into the U-tube *F*. In this way, the distillation proceeds smoothly and without interruption. A safety valve may be put in the tube *G* by means of a T-tube to prevent premature sucking over.

DISTILLATION IN VACUO USING A COLUMN STILL HEAD

Bull[47] attempted to separate, by fractional distillation in vacuo, using a column still head, a large quantity of the mixture of the methyl esters of fatty acids obtained from the fats of cod liver oil. His apparatus, which was most satisfactory, is shown in figure 70. The distilling flask, including its neck, is about 80 cm. high. Both are enclosed by a housing of thick asbestos plates and are surrounded and kept hot by the gases arising from a large Bunsen burner under the flask. The rubber stopper closing the flask, has three openings and carries a thermometer, a small silver condenser and a filling funnel, which is drawn out to a capillary and extends into the flask. The condenser, which is shown separately, consists of two parts, an outer housing closed below, and the real condenser which can be pushed up and down in it. The condenser is connected with the water system. The condensate flows from the condenser through the gauze placed in the neck of the flask, and back into the flask through the glass tubes hung in the gauze, and on its way it dephlegmates the rising vapors. The vessel receiving the distillate stands on a ground glass plate under a large bell jar. The connections with the delivery tube and the pump are established by means of a two hole stopper inserted in the tubulure of the bell jar. After the vapors have reached the top of the apparatus, the condenser is pushed into the housing, so that 2 to 3 drops condense per second, and the flame is so regulated that 1 to 2 drops of distillate are ob-

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[46] Bloch, Ignaz, and Höhn, Fritz, *Ber.*, **41**, 1979 (1908).

[47] Bull, Henrik, *Ber.*, **39**, 3570 (1906).

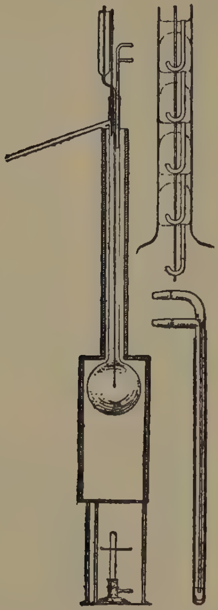

FIG. 70. DISTILLATION IN VACUUM USING COLUMN STILL HEAD (BULL)

tained per second. The neck of the flask may be protected from too much cooling by wrapping the asbestos jacket with several layers of filter paper.

DISTILLATION IN A CATHODE GLOW VACUUM, PRODUCED DIRECTLY

Vacuum distillation in the strict sense of the word had never been accomplished until Krafft solved the problem.[48] This lack of success was essentially due to two causes. As Krafft first showed, the measurement of very low pressures, or more correctly, their disappearance, by means of a mercury manometer is very uncertain, and is, therefore, entirely insufficient for true vacuum distillation, since it gives no definite indication of the reduced pressure prevailing. It is possible to determine easily and accurately, in a complete vacuum, the boiling points of only such materials as volatilize with difficulty or practically not at all without decomposition under ordinary pressures. All other substances are either gaseous at 0 mm. pressure or have the volatility of ether and chloroform which naturally greatly multiplies the difficulty of producing a high vacuum. Since manometers cannot be used to measure pressures under such conditions, Krafft connects his apparatus (fig. 71) with a Hittorf tube in which the appearance of the cathode glow indicates the disappearance of any measurable pressure, or more correctly, the attainment of a complete vacuum.[49]

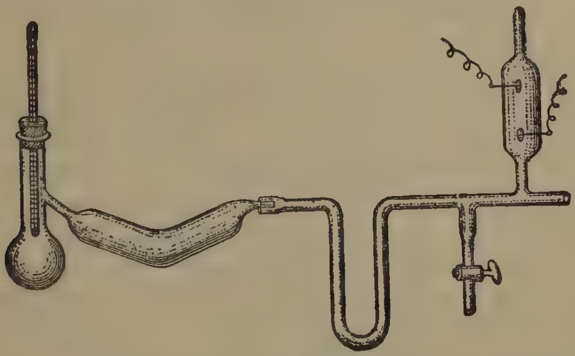

FIG. 71. DISTILLATION IN VACUUM OF THE CATHODE GLOW (KRAFFT)

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[48] Krafft, F., and Weilandt, H., *Ber.*, **29**, 1317 (1896); *Ber.*, **32**, 1623 (1899).

[49] This also is not quite correct. The cathode glow begins when the pressure is reduced to about 0.001 mm. but ceases at pressures below 0.0001 mm., when a "black vacuum" is obtained.—H. T. C.

He thought it necessary during the distillations of lactic acid, because of possible splitting out of water, to insert a calcium chloride tube containing loosely packed plugs of batting, between the distillation apparatus and the pump, in order to remove every possibility of choking by traces of vapor, which continued for a long time might produce a somewhat higher pressure in the boiling apparatus than registered by the manometer. This calcium chloride tube was omitted during the following experiments. The mercury pump works continuously and is directly connected with the receiver by a glass tube. If the receiver is cooled with ice, not enough of the vapors of substances which boil in vacuo at 100° and over, will reach the mercury pump to disturb the course of the experiment. If air and gases are entirely absent, the formation of fogs and mists, difficult to condense, and which often are very disturbing in ordinary distillations, is, of course, impossible. If the cooling is sufficient, all of the distillate, except slight traces, will remain in the receiver in the liquid or solid condition. In addition to cooling the receiver, there is an expedient to prevent the vapors going into the pump and at the same time reduce the pressure at the minimum. It consists in placing a small quantity of the substance in the receiver, and, if possible, allowing it to solidify in a thin layer on the walls. Such a layer apparently exerts a greater attraction on slight traces of vapor, particularly at the beginning of the experiment, than does the bare glass.

The Hittorf tubes for this type of distillation may be easily made from cylindrical glass tubes 6 cm. long and 2 cm. wide, into which are fused, 3 cm. apart, platinum electrodes ending in plates. Since each test lasts only a short time, this very simple apparatus may be used for a comparatively long period, though, of course, it may be replaced by better tubes. They glow when even a Bunsen element and a very small Ruhmkorff induction coil are used. As soon as the apple green cathode glow is visible on the walls of the glass, there must be present in the apparatus next to the pump, that is, in those portions lying ahead of the vapors of the boiling material, the extremely high vacuum corresponding to the cathode glow, or about one millionth of an atmosphere.

Krafft and Weilandt used a distillation flask of about 15 cc. capacity for all the satisfactory boiling point determinations cited as examples in the following discussion. The thermometer was placed 20 to 30 mm. above the boiling liquid, so that there was a column of vapor 25 to 30 mm. above the mercury bulb up to the exit tube, and the vapors rose 35 to 40 mm. higher. This arrangement was maintained also in the smooth distillations in which the neck of the flask was several centimeters higher, thus protecting the rubber stoppers. All the distillations, then, were carried out with a 60 to 70 mm. column of vapor over the thermometer bulb. The distilling flask was always connected by rubber tubing or by a ground joint, with the glass tube to which the Hittorf tube was sealed, as shown in figure 71. The reading of the vacuum was taken in the distillation space itself, thus insuring that a constant and almost negligible pressure prevailed over the distilling vapors.

TABLE 3

Boiling points at 15 mm. pressure, and under complete vacuum

SUBSTANCE	BOILING POINT IN VACUUM	BOILING POINT AT 15 MM.	DIFFERENCE
	degrees	*degrees*	*degrees*
Heptadecane $C_{17}H_{36}$	81.0	170.0	89.0
Nonadecane $C_{19}H_{40}$	111.0	193.0	82.0
Eicosane $C_{20}H_{42}$	121.0	205.0	84.0
Tricosane $C_{23}H_{48}$	142.5	234.0	91.5
Dotriacontane $C_{32}H_{66}$	205.0	310.0	105.0
Palmitic acid $C_{16}H_{32}O_2$	138–139	215.0	77.0
Stearic acid $C_{18}H_{36}O_2$	154.5–155.5	232.5	78.0
Oleic acid $C_{18}H_{34}O_2$	153.0	232.5	79.5

A sample of 3 to 4 grams was used for each determination, and the experiment was stopped as soon as only about 1 gram remained in the flask. The receiver was covered with moist bibulous paper and small pieces of ice which always sufficed to completely condense difficultly volatile materials. A few boiling points at 15 mm. pressure, and under complete vacuum are shown in table 3.

Somewhat later, Krafft[50] published additional facts regarding fractional distillation in the vacuum of the cathode glow. His receiver consisted of a very completely centralized system of 5 to 8 large, sabre shaped receptacles which were placed uniformly around a slanted axis, which also carried the upper and lower ground surfaces on which the system revolved.

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[50] Krafft, F., *Ber.*, **40**, 4779 (1907).

Vacuum distillation is particularly important from a practical standpoint, because boiling at definite temperatures even in a vacuum is attended by all the phenomena accompanying boiling under ordinary pressure. These may then be observed for even difficultly volatile materials. This follows from the fact that the molecules of a boiling substance must overcome not only the pressure of the atmosphere, but also the force of gravity, since they rise from the surface of the earth. The vapor in a vacuum is eventually saturated with respect to gravity at a definite temperature, and consequently, the temperature of the vapor in the vacuum becomes definitely fixed, just as the correspondingly higher one is when boiling occurs under measurable pressures.[51]

The influence exerted on the boiling point by the layers of vapor above a material boiling in vacuo in apparatus with high risers, may become considerable, when dealing with bodies of high molecular weight, but it is, however, only a secondary consequent phenomenon of boiling in vacuo. For example, zinc, whose vapor has a molecular weight of 65.4 begins to volatilize at 184° at 0 mm.; in a vacuum under a layer of its own vapor about 45 mm. high, it boils at 548°, and under a column 145 mm., at about 553°. This rise of boiling point, produced even in a vacuum, by supernatant layers of vapor, is relatively of little importance for materials of low molecular weight, being proportional to the molecular weight. This elevation[52] may be calculated from the published data for every substance and for every vacuum apparatus. The elevation is considerable for organic compounds of high molecular weight, such as the higher paraffins, and it should be calculated when distilling or fractionating such mixtures.

DISTILLATION BELOW 0.3 MM. MERCURY PRESSURE

Fischer and Harries[53] state that Krafft's method for vacuum distillation, just described, is very useful when distilling pure substances whose tensions are low enough at the temperature of the ordinary condensing apparatus. It fails, however, if gases or volatile liquids like ether, alcohol, or hydrocarbons are present or are produced during the operation. In addition, there is the slow working of the

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[51] Krafft, F., *Ber.*, **38**, 262 (1905).

[52] Krafft, F., *Ber.*, **32**, 1623 (1899); *Ber.*, **38**, 242 (1905).

[53] Fischer, Emil, and Harries, Carl, *Ber.*, **35**, 2158 (1902).

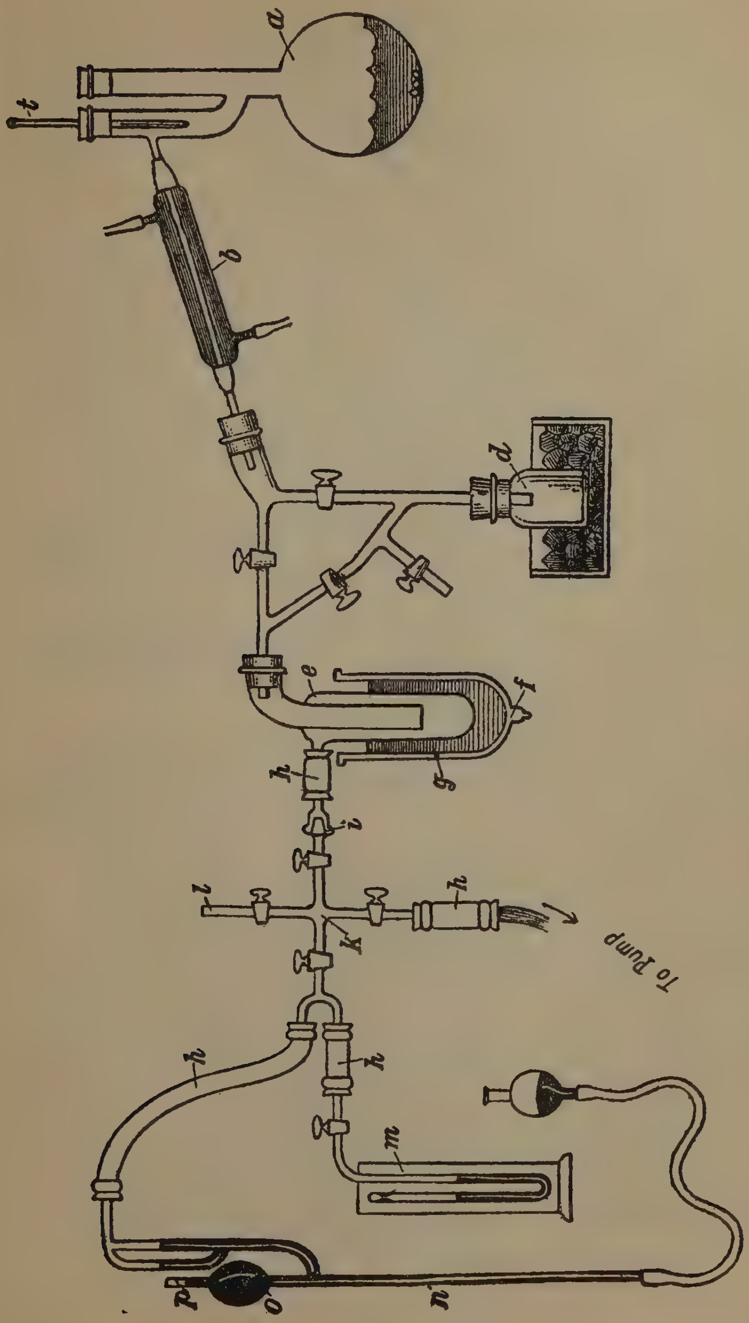

FIG. 72. DISTILLATION AT VERY LOW PRESSURE (FISCHER AND HARRIES)

mercury pump which may be a very disturbing factor when changing the receivers in fractional distillation. These difficulties are obviated in the following procedure of these investigators:

(1) By using a very powerful mechanical Geryk air pump which will evacuate an apparatus of several liters capacity, in ten minutes to about 0.15 mm. pressure.

(2) By cooling the receiver in liquid air which condenses all vapors and most gases, like ammonia, carbon dioxide, ethylene.

The air pump is driven by an electric motor and is connected with the apparatus by a lead tube, whose end is tapered so that a piece of rubber tubing may be slipped over it. When dealing with substances sensitive to overheating, the boiling vessel *a*, (fig. 72) is placed in an oil bath whose temperature is taken. The vapors escape through the side neck of the Claisen flask which it is well to cover with batting or asbestos wool to diminish the air cooling. The readings of the thermometer are not so reliable at the great dilution of the vapors as in ordinary distillations; obviously, the temperature is fixed most sharply if the distillation proceeds with comparative rapidity. It is, therefore, advisable to also control the temperature of the bath by a thermometer, if excessive superheating of the material distilling is to be avoided. Of course the temperature of the bath is higher than that of the vapors and for smooth distillations the difference should be 15 to 40°.

The condenser *b* is filled with water for higher boiling substances and with well cooled calcium chloride solution for low boiling ones. The Thorne adapter *c*, fitted with four stop cocks makes it possible to change the receiver *d* at any time without loss of vacuum. The receiver *e*, whose lead is very wide because of the danger from stoppage, serves to condense all very volatile vapors and gases. It stands in a Dewar flask *f*, filled with liquid air *g*. If gas is evolved rapidly, it is well to insert a second similar receiver. The quantity of liquid air required varies with the nature of the distillation products, but as a rule, it is very small. The glass apparatus *k*, has four cocks and connects the distillation vessels with the pump and with the devices *m* and *n*, which indicate the pressure. Air may be admitted into the system through the fourth cock *l*. At *m* is an ordinary mercury manometer. Pressures less than 1 mm. are measured by a MacLeod gauge, as slightly modified by Kahlbaum. The bulb *o* has a volume of about 50 cc., and the tube *p* is about

8 mm. internal diameter. The connections *h* are heavy rubber tubing (4 mm. bore, 10 mm. wall) which are fastened on the glass tubes with stout copper wire. The apparatus may be conveniently separated at the ground joint *i*. This may be made perfectly tight by greasing the stopper with Krafft's mixture of 1 part lanolin to 2 parts white wax. This arrangement makes the various parts of the apparatus up to the point *i* easy to loosen, but the fit is good enough to obtain a constant vacuum of 0.15 to 0.2 mm. mercury.

It is well to add two or three pieces of brick or burnt clay, the size of a bean to the boiling flask to stop the spasmodic boiling. Beyond this, the danger of bumping at the uniform pressure prevailing in the apparatus, is slight. If the joints are well closed, a distillation apparatus of about 1 liter capacity may be evacuated to approximately 0.2 mm. pressure in about 10 minutes. Figures 51 and 52 show a Geryk air pump and a vacuum meter suited to it. Several examples may serve to show the course of the distillation.

Glycerol. Distillation flask 500 cc., half filled. Pressure 0.2 mm. Temperature of bath 180°, temperature of vapors 143°. One drop distills in two to three seconds. When the receivers were changed the distillation continued quietly; in the part of the apparatus cut out, the pressure first rose to 30 mm., fell again to 0.5 mm., in three minutes, and the distillation flask could then be cut in again without disturbance.

A water condenser is not necessary when dealing with solid materials, but boiling vessels having wide glass tubes sealed to them as receivers, are used.

α-Methyl glucoside. Boiling vessel 50 cc., pressure 0.25 mm. The sublimation began at a bath temperature of 170°; but as this was very slow, a free flame was used. At 0.2 mm. the glucoside passed over without browning, leaving no residue. The temperature of the vapors was 200°. The distillate immediately solidified to a colorless crystalline mass.

This procedure was also used by Fischer in many instances, to fractionate esters of amino acids, in connection with the separation of complicated mixtures which he obtained in his very brilliant hydrolysis of protein materials. The advantage of the great decrease in the boiling point was particularly apparent, because the higher boiling esters showed marked decomposition if distillation at a pressure of 8 to 10 mm. was prolonged.

Finally, to show that even great evolution of gas does not disturb the operation, the dry distillation of crude Para caoutchouc will be described. Using 150 grams caoutchouc, and a 1000 cc. distilling flask wrapped in asbestos paper, the pressure in the apparatus remained constant at 0.25 mm. with free heating, because the gaseous products were immediately condensed by the liquid air. However, when the strongly cooled receiver was removed, the pressure in the apparatus immediately rose to 15 to 20 mm. It is easy to see that the very low pressure and the consequent rapid removal of the volatile products from the heated vessels has an essential influence on the course of the dry distillation. While Bouchardat obtained, at ordinary pressure, from 5 kgm. of caoutchouc, 250 grams isoprene, C_5H_8, 2000 grams dipentene, $C_{10}H_{16}$ and 600 grams heveene, $C_{15}H_{24}$; distillation at 0.25 mm. produced only a little isoprene and dipentene, while the main product was a mixture boiling at 180 to 300°.

If liquid air is not available, a mixture of solid carbon dioxide and ether may be used to cool the vessel *e* but, of course, the condensing action is somewhat less. If it is a question of removing water vapor, drying tubes may be employed, as was done by Krafft. The use of liquid air is preferable under all conditions, because none of the very volatile products of distillation are lost, and because the oil pump is protected from the entrance of harmful gases.

PRODUCTION OF HIGHER AND MAXIMA VACUA FOR DISTILLATION PURPOSES WITHOUT THE USE OF POWERFUL AIR PUMPS, WITH AND WITHOUT THE USE OF LIQUID AIR

Erdmann[54] has proposed the following scheme to do away with the expensive apparatus required by the procedure of Fischer and Harries. The apparatus (fig. 73) in which the vacuum distillation is to take place, is filled with carbon dioxide, and after being made air tight, a portion of its surface is cooled with liquid air. The carbon dioxide condenses rapidly, and the evacuation of a system of moderate capacity is accomplished in one minute. The tension of carbon dioxide at the temperature of liquid air is less than 0.03 mm. mercury. Carbon dioxide taken directly from cylinders may not be used, because it contains too much air. On the other hand, solid carbon dioxide obtained by rapid escape from inverted cylinders yields pure gas. This may also be obtained sufficiently pure from a Kipp apparatus. Figure 73 shows how the generator should be used. The water pump hastens the displacement of the air by carbon dioxide. The MacLeod gauge *V* is used to measure the pressure.

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[54] Erdmann, Ernst, *Ber.*, **36**, 3456 (1903).

After the apparatus of Fischer and Harries, as well as that of Erdmann, had become known, Krafft[55] again discussed vacuum distillations in detail. His views are reproduced here at considerable length, since they will be very useful to everyone who intends to carry on distillations at very low pressures. He says that in entering this field of work it is well to remember that practically never does one single procedure apply to every problem. Accordingly, the mercury pumps which are now rather widely used, occasionally are indispensable, especially in the determination of new constants, because of the convenience and certainty with which they will produce the vacuum of the green cathode glow in a perfectly tight apparatus.

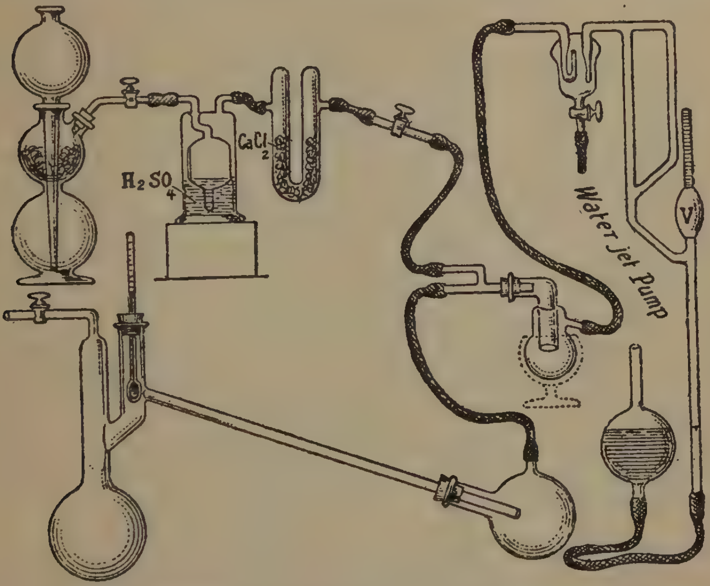

FIG. 73. VACUUM DISTILLATION WITH AID OF CARBON DIOXIDE (ERDMANN)

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[55] Krafft, F., *Ber.*, **37**, 95 (1904).

Experienced operators need not fear their fragility, at least when using the Babo pump as modified by him, which may be securely fastened to a small board or wooden stand and moved any place, since the fall tubes are now made of soft and elastic glass. He has used two such pumps for six years for a total of several thousand hours, without breaking the fall tubes. The mercury pumps are usually protected from the vapors entering from the distillation or working space, by making it absolutely air tight, since quantities of air which influence the vacuum but slightly, at once form mists, and these may be drawn into the pumps through intervening condensers. For this reason, he uses, exclusively, ground joints and cocks made tight, at room temperature, with a mixture of two parts of white wax and one of lanolin. Thermometers are either hung from the ground glass stopper provided with a hook, or are placed in a thin walled glass tube closed at the bottom, which may easily be sealed into even the smallest apparatus. The ground joints and cocks are readily put in place by slightly warming the outer portion, thus temporarily softening the sealing wax. A space of 1 to 1.5 liters can then be evacuated to the green cathode glow in twenty to thirty minutes, and during this time only a few valves need be opened, and a final regulation made at the end. The use of mercury pumps requires a certain amount of practice or expert direction, and this often deters a practical chemist from trying a single experiment in vacuo, which may possibly have been very important. This fact led Krafft to have Wittenstein[56] work out a very simple vacuum procedure available to every chemist. This required neither high powered pumps nor liquid air, and yet permitted the attainment of the vacuum of the cathode glow without the aid of any special devices.

An apparatus which has been made perfectly tight by greased ground joints and cocks is evacuated, as far as possible, by a water pump to remove the air present in it and adsorbed on the walls. This is then filled with carbon dioxide about four times, and the pressure reduced each time to 15 to 20 mm. by the water pump. The very dilute carbon dioxide remaining is practically free from air, and may be quickly removed by 50 per cent potassium hydroxide solution. The water may be removed by cooling the caustic potash solution with an ice-salt mixture, and completely condensed by solid carbon dioxide and ether. The vacuum of the cathode glow may be attained in this way in both larger and smaller apparatus, and the lye may be cut out of the system by closing a cock. The procedure is not successful without the preliminary evacuation with the water pump, because as found by Krafft, carbon dioxide will not yield a cathode vacuum unless its pressure has been reduced from 760 mm. to about 15 mm., with the simultaneous removal of about 98 per cent of the impurities.

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[56] Wittenstein, O., Dissertation, Heidelberg, 1903.

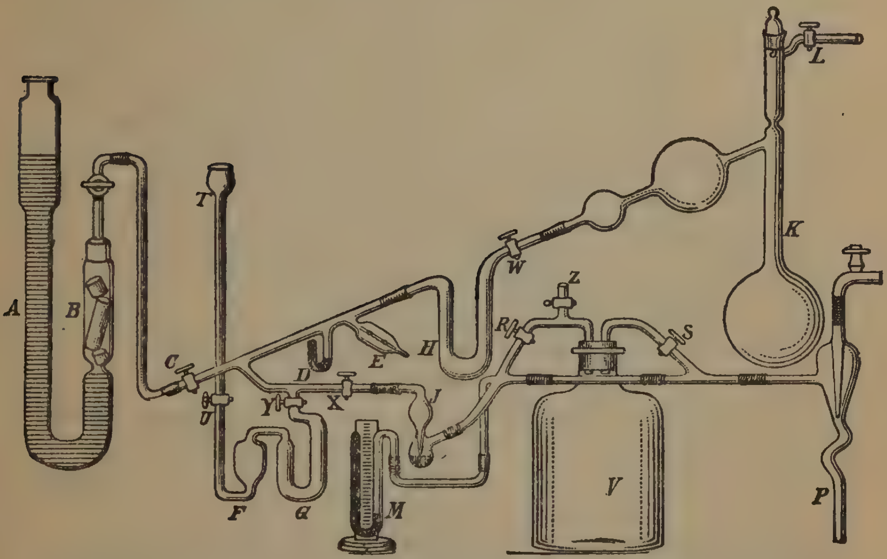

FIG. 74. PRODUCTION OF VACUUM OF CATHODE GLOW WITHOUT POWERFUL AIR PUMP AND LIQUID AIR (KRAFFT)

Figure 74 shows how the gas produced from dilute sulfuric acid and fused sodium carbonate, which usually does not need to be dried, is delivered from the carbon dioxide generator *AB*, and quickly fills the apparatus previously evacuated to 15 mm. The carbon dioxide easily expels the air from the closed narrow parts extending upward, only if the cocks at their extremities (U and L) are opened momentarily. After the whole apparatus has been filled with carbon dioxide at least four times and this removed to a pressure of 15 mm., the vessel *F* is partly filled through the funnel tube *T* with freshly boiled concentrated potash lye, which rapidly absorbs the greatly diluted residual carbon dioxide. The vacuum is controlled by a shortened manometer *D* and a Hittorf tube *E*. If the vessel *F* is cooled with a freezing mixture, the Hittorf tube shows a transient violet glow, but if it or *G*, is cooled with solid carbon dioxide and ether, a green cathode glow appears. One cylinder of liquid carbon dioxide suffices for the cooling required for ten to twelve large operations.

The evacuation of even large apparatus to the appearance of the cathode glow in *E* requires only fifteen to thirty minutes, if each removal of carbon dioxide is supported by a vacuum reservoir *V*. This is evacuated to about 20 mm., while the apparatus at the same time is being refilled with carbon dioxide from the generator *AB* (or from a cylinder if very large vessels are in use). At first the carbon dioxide is drawn off through the vacuum reservoir and the vacuum pump, but the reservoir is cut out by closing the cocks *R* and *S* as soon as the manometer *M* shows that it is no longer functioning, and the evacuation to 15 to 20 mm. is then continued by means of the pump alone. Before the water pump *P* is turned off, the cock *X* is closed and *Z* opened. The small mercury valve *J* prevents any return of gas to the inner apparatus.

An apparatus may be held together completely air tight at the ground joints, and protected against shocks by stretching elastic rubber rings over small glass projections sealed on the glass tubes at each side of every joint. In summer such apparatus will hold the vacuum of the cathode glow for hours or even days.

At the same pressures, the observations made during distillations (or sublimations) in this apparatus will, of course, agree with those for which a mercury pump has been used. Repeated use of the apparatus has shown that experienced workers prefer this method to the mercury pump for small operations. However, the latter does not require much more work than does the water pump. In some cases, such as when strong bases are being dealt with, the use of carbon dioxide is obviously impossible. The foregoing shows that a very good vacuum may be attained in suitable apparatus by evaporation of ether solutions, either with or without liquid air. It has been found that other gases or vapors such as oxygen or steam may be used to expel the air and to attain the cathode vacuum under the diminished pressure of the water pump.

STEAM DISTILLATION UNDER REDUCED PRESSURE

Steinkopf[57] was the first to pass steam through a flask arranged in the usual way for a vacuum distillation. The steam was generated in a round bottom flask provided with a boiling capillary and placed in an oil bath. Zinc and a few drops of dilute sulfuric acid were added to the water to prevent bumping. In this way, toluene, aniline, and even nitrobenzene were driven over at a very low temperature. The toluene passed over at 27 mm. pressure, the temperature of the vapor being 27.5°; the aniline at 20 mm. pressure, and 23°; the nitrobenzene at 19 mm. pressure and 22.5°. Pressure and temperature remained very constant.

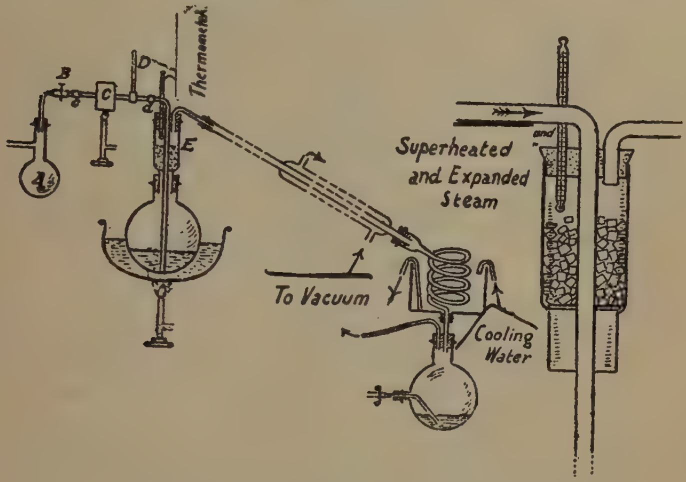

FIG. 75. STEAM DISTILLATION IN VACUUM (HARRIES)

Harries and Haarmann,[58] using a technical process of vacuum distillation with superheated steam as a guide, have devised the following perfected form for laboratory purposes. Steam at about 3 to 4 atmospheres pressure is used, and it is conveniently generated in a copper boiler fitted with a manometer. The steam is passed through the receiver *A* which must be put in to take up the condensate, and then through the throttle valve *B* into the superheater *G*. The temperature in it may be regulated by the aid of the thermometer *D* and kept at about 300°. At *cd* is a metal tube connected with the coil of the superheater and the glass connections must be plastered in at the two ends *c* and *d*. *E* is a still head filled with small glass tubes in accordance with Raschig's principle (see the previous discussion of boiling tubes), and insulated by an asbestos jacket. This still head is about 12 cm. high, 5 cm. wide, and the lower smaller ends are about 3.5 cm. in diameter. The pieces of glass tubing are kept in the proper place above the constricted portion, by a metal spiral (galvanized iron wire). The steam inlet goes through the middle of the still head and heats it. The still head controls the spurting over and foaming, otherwise inevitable during the distillation. The thermometer e^1 registers the temperature of the distilling liquids—see the enlarged sketch in figure 75.

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[57] Steinkopf, Wilhelm, *Ch. Zt.*, **32**, 517 (1908).

[58] Harries, C., and Haarmann, Reinold, *Ber.*, **51**, 788 (1918).

The distilling flask is placed in an oil bath that may be heated during the distillation. The condenser tube must be made of Jena or a similar glass to avoid breakage, and may not be cooled over its whole length with cold water. For this purpose, a portion about 70 to 80 cm. is left exposed, to act as an air condenser, and the lower portion is surrounded by a Liebig jacket, preferably made of sheet metal, one meter long. The condenser tube extends into a cooling coil, which in turn, is connected with a receiver, which has a suitable device for drawing off the condensate. If everything fits well, (cork stoppers made tight with glue and chalk are used), the vacuum is established. The valve *B* (fig. 75) must be shut off to obtain a good vacuum, and a pressure of 50 mm. or less is easily reached. To maintain the same temperature in the distilling flask as is reached in the superheater, the pressure of the steam must be reduced before entering the superheater instead of after it has passed through. If the steam is reduced behind the superheater it is greatly cooled when it expands. The result is surprising; materials now easily pass over which otherwise steam distil very slowly at ordinary pressure, no matter what the temperature of the steam. It is worthy of note that aqueous salt solutions which give up their water reluctantly, are easily freed of water by superheated steam. With the aid of this apparatus a fairly accurate fractionation of mixtures may be combined with the distillation of the material.

DISTILLATION UNDER SUPERPRESSURE

Apparatus for distillation under superpressure has not yet been constructed for laboratory purposes. Engler carried on experiments on a large scale with the apparatus devised by Krey[59] for technical practice, and starting with fatty substances, he obtained petroleum hydrocarbons. For several parallel experiments in the laboratory[60] he used glass tubes bent at an obtuse angle, and each of these, containing about 3 grams of material, was sealed. They were then placed in a digestor so that the empty arm, pointing downwards, was exposed. After heating for 4 hours at about 350°, the tubes were taken out, the gases released, and the operation repeated until the formation of a sufficiently mobile product indicated that the reaction was probably over. In this way, the reaction was carried out just as though the Krey apparatus had been used. Krämer and Spilker[61] used a wrought iron distillation kettle, provided with a regulating valve which permitted distillations at rather constant pressures up to 25 atmospheres.

DELAY IN BOILING AND FOAMING OVER OF LIQUIDS; METHODS OF PREVENTION

See the heading "Vacuum Distillation" for numerous methods of prevention.

Liquids boiling in glass or porcelain vessels frequently bump occasionally or continuously, and spurt up suddenly. The reason is a delay in the boiling instead of a regular formation of vapor with uniform heating, there is, because of the poor heat conductivity of the material, an occasional release of larger bubbles of vapor accompanied by bumping and detonations.

As was shown in the discussion of distillation under reduced pressure, a little gas generated in the liquid tends to eliminate the bumping, and consequently, the passage of air or of another gas through a liquid which boils with bumping, is an infallible remedy for this cessation of boiling even when no vacuum is being maintained.

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[59] A. Riebeck'sche Montanwerke Aktien gesellschaft in Halle a. u. Saale, German patent 37728 (1886); *Ber.*, **20** R, 32 (1887).

[60] Engler, C., *Ber.*, **21**, 1818 (1888); Engler, C., and Lehmann, Th., *Ber.*, **30**, 2365 (1897).

[61] Krämer, G., and Spilker, A., *Ber.*, **33**, 2265 (1900).

If boiling liquids precipitate solids which adhere to the bottom and produce bumping, a vigorous current of gas which hinders this deposition renders excellent service. The gas may sometimes be generated chemically without mechanical devices. Thus, Müller[62] recommends the addition of some sodium amalgam or sodium-tin alloy to the distilling liquid. Methyl alcohol, for instance, which is one of the most difficult liquids to distil because it bumps so badly, passes over smoothly if 0.6 gram of this alloy is added to 400 cc.

The writer adds zinc dust to liquids which are sufficiently alkaline (see the discussion under Kjeldahl determination of nitrogen in the division on "Analysis"). These then boil smoothly because of the favorable influence exerted by the traces of hydrogen liberated.

As a rule, it is not often possible to make use of materials which act chemically. The extreme importance of overcoming this delay in boiling, is shown by the fact that Raoult, the discoverer of the freezing point method, who in developing his ideas preceded Beckmann in efforts to make the boiling point method also practicable, did not succeed in determining molecular weights in boiling solutions, merely because he did not know how to eliminate entirely this trouble, and consequently could obtain no reliable thermometer readings. The importance of such an apparently trivial phenomenon is apparent, and the elimination of the disturbances caused by it in this case is usually considered very simple, and hardly worthy of mention after Beckmann had once discovered the remedy to be the addition of fragments of garnet and platinum tetrahedra.[63]

Faraday[64] had recommended the addition of platinum, silver, or copper wire to insure regular boiling. Kelbe[65] states that a fragment of pumice weighted with platinum wire is an almost infallible remedy. The writer has found small pieces of unglazed fire clay, fragments of unglazed porcelain plates, to be excellent for this purpose. Only a few very small fragments should be used and they are effective in all kinds of solutions. Others recommend talc, asbestos,[66] glass beads and capillary tubes. Long splinters of wood which stand in the flask and extend into the neck are useful, since they hinder both bumping and foaming because they prevent the formation of large bubbles on the bottom or on the surface.

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[62] Müller, H., *Z. anal. Ch.*, **9**, 248 (1870); *Ch. News*, **20**, 53 (1869).

[63] Beckmann, E., *Z. ph. Ch.*, **21**, 248 (1896).

[64] Faraday, *Chemical Manipulations*, 3rd ed., London, 1842, p. 205.

[65] Ziegler, A., and Kelbe, W., *Ber.*, **13**, 1401 (1880).

[66] Marquis, P., *Arch. Path. and Pharm.*, **7**, 57 (1877).

The vigorous bumping which occurs when refluxing liquids containing much sodium hydroxide, which also tend to foam badly, may according to Thiele, be avoided by imbedding the flask in iron filings.[67] The better heat conductivity accomplishes the requisite uniform distribution of the heat over the surface of the flask. Krulla[68] states that even the most concentrated caustic potash solutions will boil without bumping, if a weak electric current is passed through them. A glass tube having two platinum wires, fitted with the proper connections, passing through its closed end is immersed in these solutions.

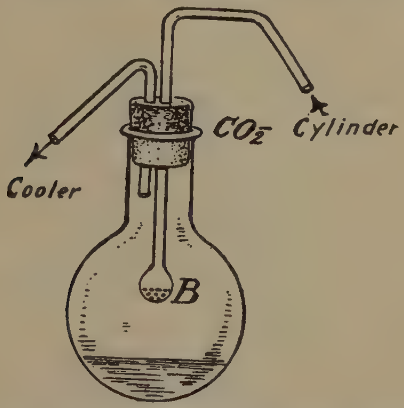

FIG. 76. AN EASY METHOD OF DISTILLING HEAVY-FOAMING LIQUIDS (KLÄNHARDT)

The most important methods of counteracting the foaming over of liquids, which otherwise cannot be distilled at all, will now be discussed. The direct distillation of strongly foaming solutions, such as aqueous solutions of saponins or of soaps, is usually extremely laborious and often impossible. This difficulty may be easily eliminated, according to Klänhardt,[69] by subjecting the surface of the liquid to a current of compressed gas, carbon dioxide, for instance. Figure 76 shows a simple device for this which has given good service in the laboratory. The real nozzle *B* is a blown glass bulb 2 cm. in diameter, provided with three rings of 1 mm. holes. Steam distillations may also be carried out smoothly in this way, as Cobenzl[70] found. His problem was to evaporate to dryness liquids which foamed very badly and were also very viscous. This had to be accomplished by means of the smallest possible quantity of heat and consequently at very reduced pressures. He was dealing with solutions of diazotized bases mixed with salt solutions. After he had exhausted his resources as to methods and apparatus, he was about to abandon the work as impossible. Klänhardt's device was tested in the same way, but in vain. Finally, success was attained through the consideration that superheated steam led over the surface of the foam would, in its efforts to become saturated, withdraw the water from the blanket of foam, and force the bubbles to break. Actually this completely overcame the difficulties. The ability to rapidly distil, with no danger of foaming over, now made it possible to prepare pure undecomposed products which had never before been obtained; or to evaporate their solutions which previously could not be evaporated without complete decomposition. Obviously, the same procedure will apply to liquids which are highly charged with gas or form gas when distilled.

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[67] Thiele, J., *Ann.*, **270**, 32 (1892).

[68] Krulla, R., *Oesterr. Ch. Zt.* [2] **12**, 62 (1909).

[69] Klänhardt, F., *Ch. Zt.*, **46**, 493 (1922).

Kunz[71] prevents bumping and foaming over of aqueous liquids during distillation by an entirely different surface treatment. He uses a little paraffin which floats on the liquid and forms a paraffin girdle 1 to 2 cm. wide next to the walls of the flask. In the center, the liquid boils quietly and with no foaming.

According to a patent,[72] foaming sugar solutions are prevented from boiling over while being concentrated, by the addition of a mixture obtained by stirring together vegetable fats and sulfuric acid. This is claimed to be more efficacious than the addition of fat alone.

It is not very well known that the foam on cold liquids, arising either from the generation of carbon dioxide or from shaking strongly alkaline liquids, is immediately broken by adding a little ether.[73]

[70] Cobenzl, A., *Ch. Zt.*, **46**, 630 (1922).

[71] Kunz, H., *Arch. Pharm.*, **225**, 632 (1887).

[72] D'heury, L., German patent 300 (1877); *Wagner Jahresbericht*, **24**, 803 (1878).

[73] Butyl alcohol, and especially ethyl acetate, are even more effective. —H. T. C.

CHAPTER V

DIALYSIS

Dialysis is a process for removing crystallizable materials from a solution containing both crystallizable and non-crystallizable bodies. As is well known, it is based upon the fact that the former, when dissolved, diffuse through membranes, while the latter do not. Originally, animal bladders were used as membranes, but this is no longer the case, parchment paper being now used exclusively. Since animal bladders are never perfectly uniform, traces of colloidal materials pass through them. This does not occur with parchment.

Dialysis carried out in tubes is more rapid. Such tubes are on the market, and were first made during the war period of 1870 as skins for "Erbswurst." If such a skin containing a solution of sodium chloride, for example is fastened as shown in figure 78, then hung in a cylinder, none of the solution will penetrate to the outside. However, if the cylinder is filled with water, osmosis will begin, and the exchange between the salt in the skin and the outer water will continue until the salt solution is of the same strength both within and without. If the tube contains also some non-diffusing material, like egg albumen, this will remain in the solution within, so that in this way it is possible, by renewing the outer water, to finally remove all of the salt from within the tube. Since all naturally occurring albumen solutions contain dissolved salts, this method is used frequently because it is the only practicable one for removing the crystallizable salts present in albumen solutions.

The following methods of dialysis are most used at present. The earliest and simplest is due to Graham,[1] who was the first to really study the phenomena accompanying dialysis. In this method, the dialyzer is nothing but a flat vessel with a parchment bottom (fig. 77). This is floated on the liquid, which almost always is water. After a certain time, when there is much liquid in the outer vessel as compared with the inner, a large part of the crystallizable body has passed into the outer water. The following may be used as a norm of the process: the diffusion is accelerated by using a rather large membrane, and the heavier liquid is placed in the *dialyzer* which hangs in the water in such a way that the membrane is not pressed inward. Frequent renewal of the outer water is necessary for the quantitative removal of the salts originally present in the dialyzer *A*, making this otherwise simple method inconvenient and time consuming.

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[1] Graham, T., *J. Ch. Soc.*, **3**, 257 (1850).

Higher temperatures and frequent gentle shaking accelerate the dialysis of water solutions. Since the process slows down as the content of diffusing material decreases, it is well, after some time, to boil down the aqueous contents of *A*, and to dialyze anew. Double sided *dialyzers* may also be used to hasten the process. The water for these is held in a preparation glass of suitable size as shown in figure 78a.

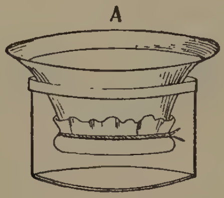

FIG. 77. DIALYZER

Since tubes of parchment paper are available, these are now usually used because they permit uninterrupted flow of the outer water, thus producing a sort of washing out of the soluble salts. For this purpose, a high cylinder with a shoulder should be used, since its height determines the active length of the dialyzing tube (fig. 78b). The parchment tube filed with the liquid to be dialyzed is fastened at both ends to a glass rod laid across the shoulder of the cylinder. The cylinder is filled with water and more allowed to drop into it continuously from the water supply. It runs off from the bottom, and the pinch clamp on the rubber tube *G*, is properly adjusted for this. Emptying from the lower part of the cylinder has the advantage, that the liquid weighted with salt runs off from the lowest point. If the dialysis is made in a similar cylinder, but closed at the bottom, the water must be run in at the bottom by means of a glass tube, and allowed to overflow at the top. In this case, the heavier liquid layers, rich in salt, must be carried upward. However, good dialysis may be accomplished by this latter method, so that a cylinder having an opening near the bottom is not absolutely assential. After the dialysis against tap water has continued long enough as shown by testing the outer water with a suitable reagent, the cylinder is filled with distilled water several times, and in this way, it is easy to wash the content of the tube free of chloride and sulfate.

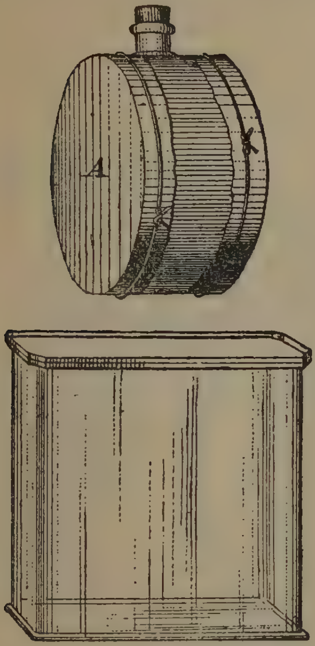

FIG. 78a. BILATERAL DIALYZER

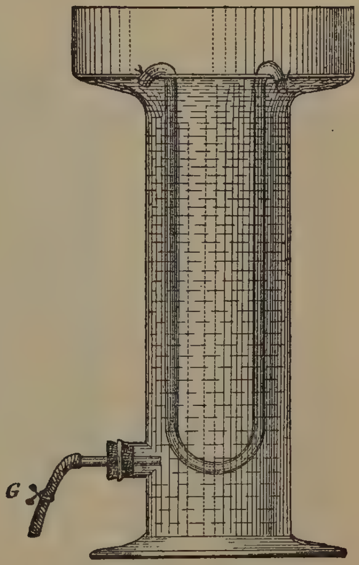

FIG. 78b. TUBE DIALYZER

RAPID DIALYZERS

Thoms[2] has constructed a rapid dialyzer. In this, the liquid to be dialyzed and the water is placed in separate closed chambers and are made to glide regularly over the membranes by means of a shaking apparatus. Gutbier, Huber and Schieber[3] have also constructed a rapid dialyzer and their general, valuable views on dialysis are given here.

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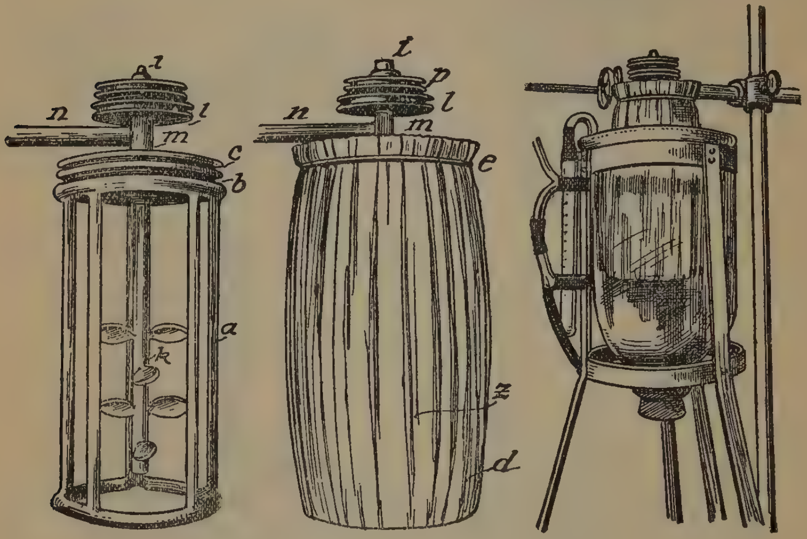
[2] Thoms, H., *Ber.*, 50, 1236 (1917).

[3] Gutbier, A., Huber, J., and Schieber, W., *Ber.*, 55, 1518 (1922).

While investigating protective colloids they often met the problem of thoroughly dialyzing the electrolytes from large quantities of colloidal solutions in the shortest time possible. No known device met the requirements established by the character of their protective colloids. The consideration that a given system rich in electrolytes may be purified by dialysis more rapidly the greater the extent of the membrane surface, and the greater the difference in concentration between the inner liquid and the outer water led them to design a rapid dialyzer. It is shown in figure 79, *a*, *b*, *c*. A revolving unit *a* is held by glass columns and fastened to the wooden disk *b*. The membrane *d* is fastened by a cord *e* in the groove *c* running around the disk. The membrane covers *a* so that it envelopes the whole supporting structure from the bottom up, like a sack, and lies around the wooden ring in natural folds *z*. This makes the membrane surface as large as possible and also brings about an intimate contact of the inner liquid with the outer water, which must strike into the folds when the unit is rotated. Parchment paper, designed for dialysis, is used as the membrane. The wood disk *b* is provided with a neck extending up-



a *b* *c*

Fig. 79. Rapid Dialyzer (Gutbier)

ward on which are fastened the rotating devices in such a way that an external shaft, carrying a driving wheel *l* makes possible the rotation of *a*. The shaft *i* of the stirrer *k* passes through the internal opening of the outer shaft. The driving wheel *p* which is wedged to *i*, serves to turn the stirrer. The bearing holder *m* surrounds the outer shaft. It may be fastened to any desired support by means of the boom *n*. The rotating unit closed by the membrane is put into a glass vessel, preferably a tubulated bell jar, which holds the outer water. This is continuously renewed from the large supply tank placed above, and, if occasion demands, may be brought to a definite temperature by heating or cooling coils placed in the jar. Tubulated bell jars 25 cm. high, 20 cm. in diameter have been found suitable for dialyzing vessels for the measurements which this revolving dialyzer has made available for scientific purposes. The outer water is led into the bottom through the tubulature from the supply tank by means of a glass tube drawn out to a rather coarse point. The jar stands with the upper thickened edge in a frame of sheet iron and may be firmly fastened in place by a wing nut. The outer water is drawn off by a waste syphon so that the water in the jar can be made to stand at any height corresponding to the level of the inner liquid. The syphon which may be conveniently fastened to the stand with two pipe hangers is a glass tube (like a test tube), 15 mm. in diameter, and narrowed at the top. On one side, near the upper end, there is sealed a fork consisting of two glass tubes 6 mm. in diameter, bent away from each other. An inverted glass tube 6 mm. wide and having an arm 20 cm. long, is fastened in the tube and made tight with rubber tubing. The water flows off through the lower part of the fork, and the syphon is filled through the upper part. The height of the liquid is easily established by raising or lowering the syphon.

The dialyzer is filled by pouring the liquid through a hole in the wood block *b*, while water is being run into the bell jar. The unit *a* and the shaft *i* are rotated in opposite directions by the driving mechanisms. A small electric motor with a connecting gearing is best for driving the rotating unit and the stirrer. The size of the gearing is so chosen that the system may be rotated 50, 100 or 150 r.p.m. The apparatus was tested out to determine the velocity of dialysis with various liquids—solutions of electrolytes, colloid systems and mixtures of colloids and ionic dispersoids—and the results compared with those given by the dialyzers most commonly used. These comparisons showed: (1) a higher velocity of dialysis than was ever attained before; (2) excellent protection of the inner liquid from the atmosphere, yet permitting easy removal of test portions; (3) hindering the dilution of the inner liquid; (4) great certainty of action because a single piece of parchment satisfies a large range of requirements; (5) uninterrupted change of the outer water; (6) accomplishment of the dialysis at elevated or lowered temperatures, without the aid of complicated devices.

Golodetz[4] has devised an apparatus for the quantitative dialysis of small quantities of liquids. Its purpose was the separation, in an almost unchanged condition, of the diffusible materials, such as mineral salts, sugars, crystallizable bases, etc., contained in such physiological substances as blood, milk, animal organs and secretions, or in foods. Using parchment paper tubes, five to seven hours dialysis was sufficient in almost all cases, to obtain 98 to 99 per cent of the dialyzable constituents. To determine when the dialysis is finished small portions are removed from the dialyzing cylinder from time to time after several hours' dialysis, and they are tested for evaporation residue, or a given constituent is sought.[5]

[4] Golodetz, A., *Ch. Zt.*, **37**, 259 (1913).

[5] A technique involving collodion membranes has been worked out by Kober (*J. Amer. Chem. Soc.*, **39**, 944 (1917); **40**, 1226 (1918)).—H. T. C.

CHAPTER VI

Passage of Vapors Through Hot Tubes

The vapors and gases produced during distillations are sometimes passed through hot tubes before they enter the condenser. If they are to pass only once through a hot tube, an iron tube is heated, or if chemical reactions are to be considered, a glass tube is heated in a combustion furnace, and the vapors led through it.

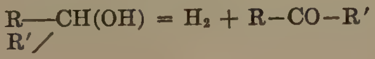
Lüddens[1] thinks it an advantage to pass carbon dioxide through the tube along with the vapors to facilitate their passage. When he did this with benzene vapors, he obtained diphenyl without the separation of much carbon.

$$2\,C_6H_6 = C_6H_5-H_5C_6 + H_2$$

Ipatiew,[2] particularly, has pointed out that in pyrogenetic reactions, the walls of the vessel may often influence the course of the reaction, the decomposition and character of the decomposition products, because of contact action. The temperature of the tubes was measured with a Le Chatelier pyrometer. He heated the glass tubes to 660 to 700°, the iron ones to 720 to 800°. In this way, methyl alcohol, in iron tubes, produced about 25 per cent formaldehyde. Ethyl alcohol was decomposed little in glass tubes, but he obtained acetaldehyde, paraldehyde and water, together with combustible gases, in an iron tube. Isoamyl alcohol gave 30 to 40 per cent isovaleraldehyde. Thus, the decomposition of primary alcohols proceeds to a considerable measure in accordance with the equation:

$$R\cdot CH_2OH = H_2 + R\cdot CHO$$

Secondary alcohols produce ketones



$$\begin{array}{l} R\!\!-\!\!\!-CH(OH) = H_2 + R-CO-R' \\ R'\diagup \end{array}$$

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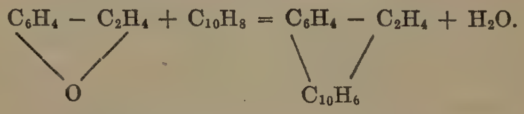
[1] Lüddens, H., *Ber.*, **8**, 870 (1875).

[2] Ipatiew, W., *Ber.*, **34**, 596 and 3587 (1901).

Tertiary alcohols are attacked very little. He assumes that those metals which readily decompose water and consequently are easily oxidized, particularly facilitate the decomposition of alcohols into aldehyde and hydrogen. He later[3] extended his experiments very considerably by passing the vapors of various alcohols over a large variety of hot materials to study their contact action.

Thiele,[4] continuing a study by Caventou,[5] produced butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, by distilling 300 to 400 grams of amyl alcohol, in the course of an hour, through an iron tube, 40 mm. wide, heated to a medium red over 40 cm. of its length. The vapors formed passed through a colled flask, a reflux condenser, and then through another flask cooled with ice, and they then entered a large bulb apparatus containing undiluted bromine cooled with ice. If the distillation proceeds properly no finely divided carbon or naphthalene, or thick black tar, will be seen in the condenser. The volume of the bromine gradually increases greatly, and the bromides are finally light brown. Otherwise, the temperature is too high or the distillation too slow.

Krämer and Spilker[6] recommend a two armed tube of the form shown in figure 80. The lower arm is heated in a combustion furnace, while the upper one serves as a preheater. At dark red heat, for example, it permits coumarone vapor to pass through undecomposed, but, on the other hand, water is split out when coumarone and naphthalene vapor are passed through together, forming chrysene:



$$\underset{\diagdown\ O\ \diagup}{C_6H_4 - C_2H_4} + C_{10}H_8 = \underset{\diagdown\ C_{10}H_6\ \diagup}{C_6H_4 - C_2H_4} + H_2O.$$

Gräbe[7] found that no phenanthridine was formed when benzylidene aniline, $C_6H_5{\cdot}CH{:}N{\cdot}C_6H_5$, was passed through glass tubes heated to dull redness, but Pictet and Ankersmit[8] obtained this material when they passed benzylidene aniline through an iron tube filled with pumice fragments, and heated to bright redness.

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[3] Ipatiew, W., *Ber.*, **35**, 1047 (1902).

[4] Thiele, J., *Ann.*, **308**, 337 (1899).

[5] Caventou, E., *Ann.*, **127**, 93 (1863); *C. R.*, **56**, 646 (1863).

[6] Krämer, G., and Spilker, A., *Ber.*, **23**, 84 (1890).

[7] Gräbe, C., *Ber.*, **17**, 1370 (1884).

[8] Pictet, Amé, and Ankersmit, H. J., *Ber.*, **22**, 3340 (1889).

Nef[9] carried out very accurate experiments in glass tubes. He passed 20 grams of methyl alcohol, free from acetone, through a combustion tube filled with pumice, at 610 to 630°, in one hour. Most of the product is gaseous, and in addition, 5 cc. of an aqueous solution of formaldehyde was obtained, in agreement with Ipatiew's results. When he added 100 grams of zinc chloride to 40 grams of pumice and heated to only 400°, gaseous products alone were obtained. On mixing 47 grams phosphorus pentoxide with 27 grams pumice he again obtained only gaseous products at 400°, but much carbon separated in the tube, which could be ascribed to the dissociation of the formaldehyde primarily formed. He also extensively re-investigated the behavior of acetaldehyde, propyl alcohol, etc.

Schmidlin[10] showed that approximately a 14 per cent yield of ketene is obtained by passing acetone vapor through a glass tube heated in an ordinary combustion furnace to about 500 to 600°. The gaseous ketene is recovered as a liquid by cooling the gaseous mixture in a carbon dioxide-ether mixture:

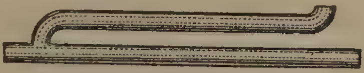

FIG. 80. HOT TUBE (KRÄMER AND SPILKER)

$$2\ CH_3{\cdot}CO{\cdot}CH_3 = 2\ CH_2{:}CO + 2\ CH_4$$

If vapors are to be passed through hot tubes repeatedly, because one passage is not sufficient, a device somewhat similar to the one recommended by La Coste and Sorger[11] is used. In this apparatus, it is possible continuously to expose benzene vapor, for example, to a high heat for weeks at a time. The benzene is heated in a large flask A (fig. 81). The flask is closed by a three-hole rubber stopper, and a lead tube, whose end is cut off at an angle, passes through one opening and ends in the neck of the flask above the liquid. The upper end of this tube is soldered in the form of a T into a short, rather wide lead tube, open at both ends. While the apparatus is in use, one end of the latter tube is closed by a glass stopper fitted with a rubber ring. An iron tube, 1.5 meters long and 2 cm. wide, is luted into the other end, and it may be heated to glowing in a combustion furnace slanted upward. This tube is bent sharply downward near the place where it leaves the furnace and is soldered into the side tube of a lead receiver. The part of the tube lying between the furnace and receiver is well cooled by sprinkling water over it to prevent melting off the lead side arm. The receiver is a short lead cylinder about 30 cm. long and 6 cm. diameter, closed at both ends. In addition to the lead side arm in the middle, mentioned above, it has another side tube of equal width on the opposite side, into which is fitted a condenser extending upward at an angle and through which the gases evolved must pass. A third narrower lead tube about 70 cm. long is soldered into the bottom of the receiver. Another lead tube of the same width is fastened to this by a coupling, and ends just above the bottom of the flask, and carries the condensed vapors back to it. The flask, in addition, is connected with a second empty safety flask, by a double right angled glass tube which extends almost to the bottom of both flasks. From the upper end of the condenser, a long glass tube leads downward to a second safety flask which in turn is connected with a wash bottle half filled with water, through which the gases must escape.

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[9] Nef, J. U., *Ann.*, **318**, 195 (1901).

[10] Schmidlin, Julius, and Bergman, Maximilian, *Ber.*, **43**, 2821 (1910).

[11] La Coste, W., and Sorger, C., *Ann.*, **230**, 5 (1885).

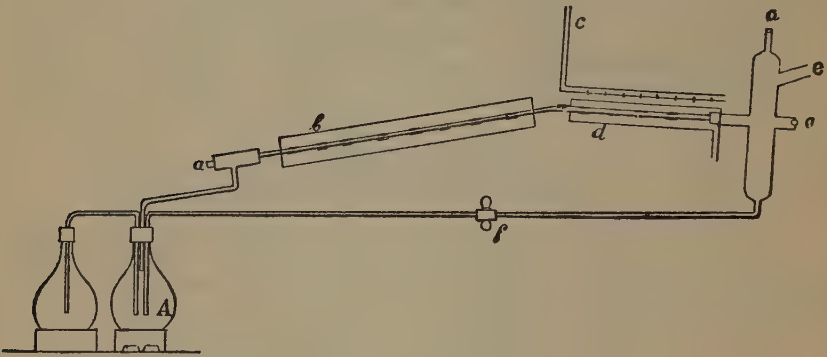

FIG. 81. APPARATUS FOR CONTINUOUS HEATING OF GASES AND VAPORS (LA COSTE)

SEALING CORKS, GROUND-GLASS SURFACES AND COCKS

Cork stoppers may be perfectly sealed for even vacuum distillations by coating them with thick collodion solution after they have been put in place. If corks are used with reflux condensers, and the extraction medium takes up soluble materials from them, they should be covered with tin or lead foil glued to them (see heading "Extraction"). Picein may also be used as a seal, either with or without corks.[12] This black material, sold in sticks like sealing wax, adheres to glass, metal, wood, etc., particularly when slightly warmed, and is not brittle. Corks to be used at higher temperatures are made impermeable by means of a glue solution thickened with chalk.

Cocks[13] are lubricated with a mixture of white wax and Adeps lanae (for room temperature 2:1); or one part of white wax is melted with three parts neat's foot oil. A mixture of beeswax, lanolin and fat, which may be prepared in any desired degree of hardness, gives off so little gas,[14] that with a good pump a pressure of less than 0.001 mm. of mercury may always be easily attained, even though there are many cocks in the apparatus. Aluminium oleate has the desirable characteristic that its lubricating qualities do not decrease, even when cocks or desiccator lids are pressed into position. Viscous mixtures of aluminum oleate and beeswax form particularly resistant seals.[15] Anhydrous lanolin seals desiccators so well that they will remain tight for weeks. Cocks may be sealed when desired with syrupy phosphoric acid. Ground surfaces may be tightened by forcibly rubbing them together for some time with a paste of finely pulverized and elutriated emery and glycerine.

Caoutchouc dissolved in carbon tetrachloride may be used to prepare caoutchouc coatings. According to Norrenberg, it is necessary, when preparing such solutions, first to barely cover the natural caoutchouc with the solvent. After two hours it will have swelled greatly, and have absorbed all the solvent. This procedure is repeated until the swollen caoutchouc forms a gelatinous mass, and then the addition of the solvent may be more rapid. One kilogram carbon tetrachloride with 50 grams of caoutchouc forms a liquid which is most useful for sealing apparatus.

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[12] Jorissen, W., *Z. angew. Ch.*, **26**, 637 (1913).

[13] Krafft, F., and Weilandt, H., *Ber.*, **29**, 1322 (1896).

[14] Paneth, Fritz, Matthies, Max, and Schmidt-Hebbel, Edgar, *Ber.*, **55**, 780 (1922).

[15] Wiechowski, W., *Münchener med. Wochenschrift*, **68**, 1083 (1921); *Chem. Zentr.*, **92**, IV, 1163 (1921).

If ground surfaces are to be highly heated, fats cannot be used for tightening them. In such cases, small ground surfaces should be most carefully prepared according to Kempf's[16] method. These are rubbed-in with graphite, which is most simply done by stroking them with a medium hard lead pencil.

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[16] Kempf, R., *J. pr. Ch.*, [2] 78, 207 (1908).

CHAPTER VII

EVAPORATION IN VACUO

Small quantities of liquids to be evaporated in vacuo, are allowed to stand at room temperature in evacuated desiccators (see later the heading "Drying of Solid Materials, etc."). However, there are desiccators fitted with a dish, in which the material may be boiled, and therefore, directly evaporated under reduced pressure. Anschütz[1] and also Brühl[2] have described such devices.

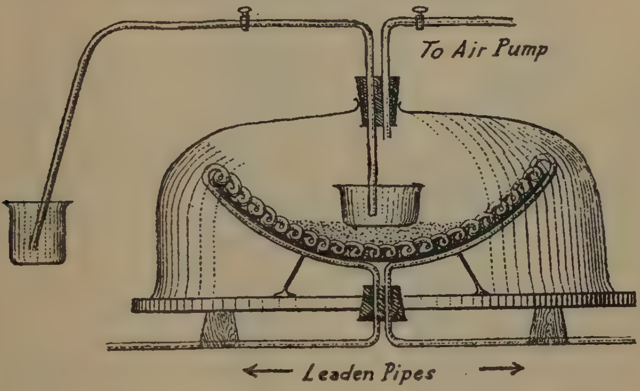

FIG. 82. VACUUM EVAPORATION APPARATUS (LASSAR-COHN)

The writer has used the apparatus shown in figure 82 which is simply constructed and can be heated. The very strong glass plate which is ground to fit a large bell jar, has a hole in the center. A porcelain dish set on a small tripod is placed just above the two-hole rubber stopper closing the opening. A lead tube of the proper size passes through one opening of the stopper, and is coiled around the inside of the dish—the individual coils are fastened together with wire—and the tube then led out through the other opening of the stopper. Copper powder, such as is obtained by the reduction of copper oxide, is put into the dish to transfer the heat better and the heating is accomplished by passing hot water or steam through the lead tube. Small dishes containing sulfuric acid may be placed under the tripod. The lead tubes make it necessary to elevate the apparatus on two wooden blocks. The air is drawn off through a tube passing

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[1] Anschütz, R., *Ann.*, **228**, 305 (1885).

[2] Brühl, J. W., *Ber.*, **24**, 2458 (1891).

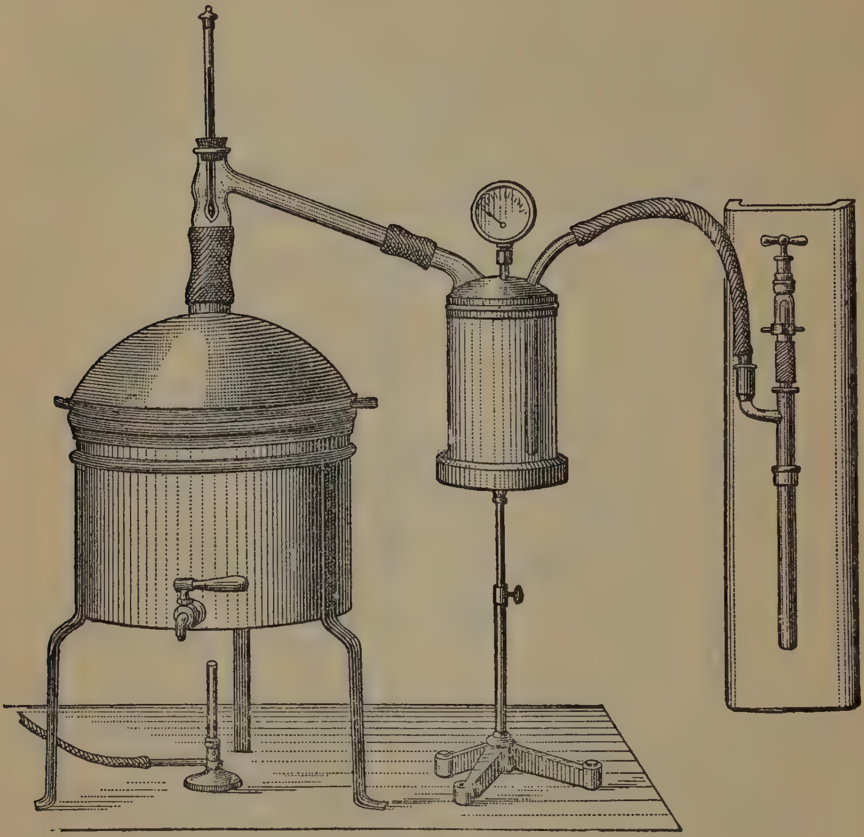

FIG. 83. VACUUM EVAPORATION APPARATUS (ALTMANN)

through the upper opening of the bell jar. A second glass tube, provided with a stop cock, dips into an adjacent beaker. When the cock is opened, the liquid is forced in by the external air pressure, and thus the dish standing under reduced pressure may be filled without interrupting the process. This latter arrangement is due to Walter,[3] who also has devised apparatus for evaporating liquids in dishes under reduced pressure, but these are more complicated. Occasionally the contents of the dish spatter; if this happens, a slow current of air passed through the liquid overcomes the difficulty as in vacuum distillations. For the evaporation of larger quantities, it is necessary to use apparatus corresponding to that used in factory practice. This may be purchased complete with all accessories. An apparatus of this type is shown in figure 83. The evaporation is carried on in a bath, provided with a thermometer which shows whether the desired low temperature is maintained. In the form illustrated, the concentration of the liquid occurs in a porcelain dish, the dome being made of glass so that there is no chance of contaminating the evaporating material by metal.

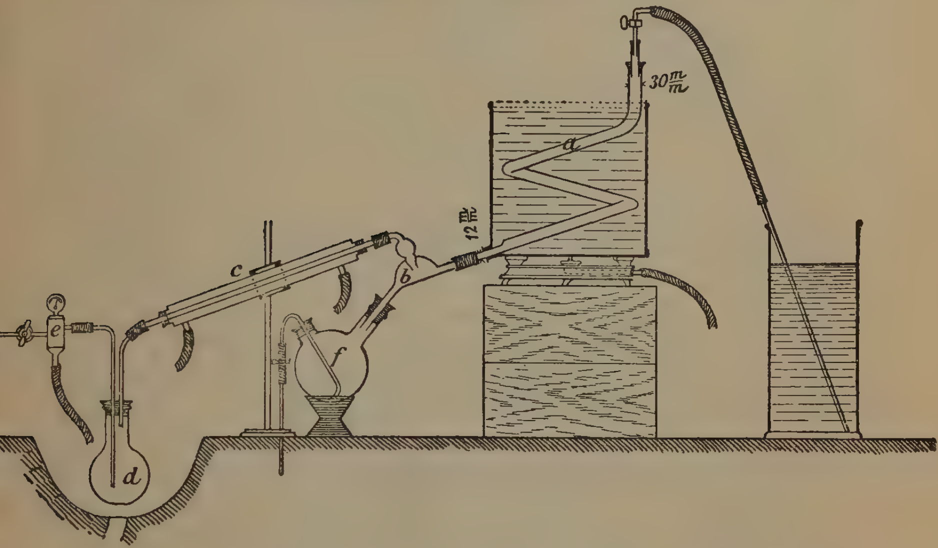

FIG. 84. VACUUM EVAPORATION APPARATUS (SCHULZE AND TOLLENS)

This method of concentrating in a vacuum requires that the material be heated for a long time. In general, the dissolved materials are not harmed by this, though there are some exceptions. Schulze and Tollens[4] have constructed a special apparatus permitting the most rapid possible evaporation, with lowering of the boiling point, of liquids which decompose easily, or of solutions containing materials (such as sugar) easily decomposed by heat. The arrangement of the apparatus is as follows (fig. 84): The liquid to be evaporated is drawn from an adjacent vessel by a syphon-like glass tube provided with a stop cock, into the copper coil *a* which is heated in the water bath. The velocity of the stream may be regulated by the cock, and it may be observed through the glass projection at the end of the copper coil. A vacuum is maintained in the copper tube by a water pump. The greater part of the water evaporates as it passes through the copper tube, and is removed by the air pump following the path *b*, *c*, *d*, *e*. The concentrated liquid which has been exposed to the heat of the water bath for only a very short time, flows through the glass tube *b* into the air-tight receiver *f*. The receiver *f* may be emptied, when desired, by means of a syphon, after the air has been admitted. The flask *d* connected air-tight with the condenser *c* and the pump *e* is evacuated continuously and cooled at the same time. The apparatus can concentrate, in one hour, 4 to 5 liters of a mobile liquid to 1 liter. It is best not to concentrate to a syrup because the flow of the solutions then becomes too sluggish. It seems to the writer that this apparatus should be of particular interest to biochemical laboratories. If it were so modified that the copper coil which would have to be lengthened, could be heated in boiling ether vapor, it would then be possible to concentrate, without danger, solutions of albumen, whose concentration otherwise is only possible at the expense of much patience, by allowing them to stand adjacent to dehydrating agents in unheated, evacuated desiccators.

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[3] Walter, J., *J. pr. Ch.*, **140**, 425 (1885).

[4] Schulze, C., and Tollens, B., *Ann.*, **271**, 46 (1892).

CHAPTER VIII

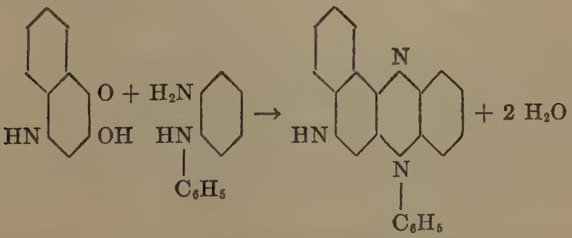
SEALED TUBES

FILLING AND CLOSING SEALED TUBES

Their replacement by covering the materials with copper

If materials are to react with each other at a temperature higher than that permitted by the volatility of one of them, the reaction must usually take place in closed apparatus. Often a slight elevation of temperature and pressure is sufficient, and in such cases, capped soda pop bottles may be used. They are heated by wrapping them in straw, or a cloth, and placing them in cold water which is then slowly brought to a boil. It is not wise to use temperatures higher than that of boiling water, although they are easily available by adding salt or calcium chloride (see heading "Baths") since the seals will not stay tight.

Regarding the use of pressure flasks, Kehrmann and Messinger[1] cite the fact that hydroxynaphtho-quinoneimide and amino-diphenyl-amine condense very slowly at room temperature, but that the synthesis of roseinduline from these materials proceeds smoothly at even slightly increased pressure and temperature. Consequently, they heated 5 gm. hydroxynaphtho-quinoneimide with an equal molar quantity of amino-diphenyl-amine, 5 cc. glacial acetic acid and 300 cc. alcohol in pressure flasks, for forty-eight hours in boiling water, and through this slight increase in pressure they accomplished the synthesis of the roseinduline.



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[1] Kehrmann, Fr., and Messinger, J., *Ber.*, **24**, 587 (1891).

In the majority of cases in the laboratory, however, sealed tubes are used (fig. 85).

These sealed tubes, if properly handled, will withstand considerable pressure without bursting. Potash glass is usually preferred to soda glass for making them, though it is not essential. Even potash glass is not entirely unattacked, especially by water at high temperatures. Hoppe-Seyler[2] states that after heating a sealed tube 30 cm. long, made of the best potash glass, and containing water at 180 to 200° for six hours, the inner surface of the tube was covered with a white coating, and the water had taken up a small, but de-

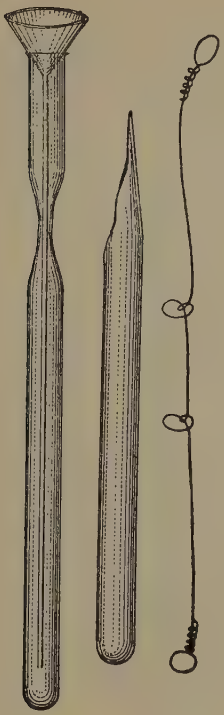

Fig. 85. Sealed Tube

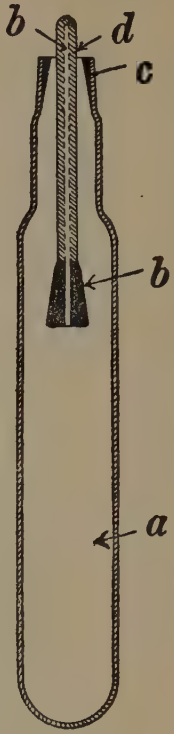

Fig. 86. Sealed Tube with Pressure Seal (Kleinmann)

[2] Hoppe-Seyler, F., *Z. physiol. Ch.*, **13**, 73 (1889); Foerster, F., *Ber.*, **25**, 2494 (1892).

cided quantity of alkali. Accordingly, if it is necessary to heat a very strong alkali, such as soda lime, in a tube, it is better to place it, and the materials to be mixed with it, in a test tube, which in turn is placed in the sealed tube.

Solids are put into tubes closed at one end and the tubes are then sealed. To avoid contamination of the part which is to be sealed later, it is better to weigh out the solid material into a narrow test tube, and then slide it into the tube. To facilitate subsequent mixing of solids with liquids in the tube, they are mixed with dry salt or similar material.[3] When liquids are to be put into the tubes, the end of the tube to be sealed is first drawn out somewhat, and then the liquid added through a funnel with a long, thin neck. The anticipated pressure determines how far the tubes should be filled. When withdrawing the funnel, it is necessary to carefully avoid contaminating the wall of the tube at the place to be sealed, or it may be impossible to make the seal. The seal is made by rapidly rotating the constricted portion in the blast lamp flame and allowing it to fall together to a capillary point, pulling it as little as possible. When Dimroth[4] attempted to prepare 1-phenyl-2, 3-triazole, he heated 20 grams acetone, saturated at 0° with pure dry acetylene, with 1 gram of phenylazide in a sealed tube for forty hours in a boiling water bath, and found it difficult to seal the tubes containing acetylene because the glass was made brittle by the finely divided carbon separating from the acetylene. Therefore, he displaced the acetylene from the gas space by carbon dioxide.

Kleinmann has devised a bomb tube with a conical ground glass seal, based on the principle of the pressure seal (fig. 86). The reaction chamber of the tube is *a*, *b* is the ground-glass conical seal, and *d* the glass extension of the sealing cone. The capillary *h* is provided with an opening running into the cone *b*. The sealing cone *b* fits air tight into the ground glass seat *c*. After the material has been placed in the reaction chamber *a*, the tube is closed by raising the cone *b* into the ground glass seat *c*. As the pressure generated by the reaction increases, the cone is pressed more firmly into the seat. If no pressure, or even diminished pressure, is present, in the tube after the reaction is over, the tube may be opened by simply pushing *b* downward. If there is pressure in the tube, the closed end of the head of the capillary is first blown open by heating it until it melts. In this case, the small hole must be resealed before the tube may be used again.

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[3] Merz, V., and Paschkowesky, S., *J. pr. Ch.* [2], **48**, 456 (1893).

[4] Dimroth, Otto, and Fester, Gustav, *Ber.*, **43**, 2222 (1910).

Very great pressures often develop when the tubes are heated and many of them break. They must always be handled cautiously because great pressure may exist in them, even after they have cooled, and so they may be dangerous while being opened. All of these points will be discussed in detail later, together with the various methods of avoiding, or at least lessening, these dangers.

The unique procedure of Wolfson[5] will now be discussed. The substance to be heated is not sealed in glass tubes, but is coated with electrolytically precipitated copper and then heated. For the sake of clarity, it seems advisable to give his views which indicate that this process may occasionally be useful, or perhaps it may be modified for other purposes. If materials are to be heated to a temperature higher than their boiling points, or if reactions are expected to produce low boiling by-products, it is the general practice to use sealed tubes, glass vessels with pressure seals, or metal autoclaves. The disadvantages of all these are well known. Sealed tubes have only a small capacity and break easily if the pressure rises considerably. Pressure bottles have a large capacity, but they are dangerous to open if the internal pressure is high. Metal autoclaves are expensive and demand careful handling if they are to remain in good condition.

Wolfson proposes to overcome these difficulties by enveloping the substances themselves, that is, without enclosing them in vessels, by a metal covering deposited electrolytically. These metal envelopes serve as containers for the substance to be heated. They can resist any desired internal pressure, since the thickness of the covering can be varied with the degree of heating and with the anticipated internal pressure. In other words, if the reaction mass is to be heated slightly and the internal pressure is to be low, a thin metal covering is electrolytically deposited, but a thick one must be formed if the heating is to be strong and the pressure high. For instance, if a mixture of two solids, or of one solid and one liquid material, is to be heated to 300° they are kneaded together, with the addition of heated paraffin if necessary, allowed to cool and formed into a four cornered tablet. Or the mixture may be formed into a plastic magma by the addition of another suitable chemically indifferent material, and then coated with paraffin. The surface of the tablet is made a conductor for the electric current by the usual method—such as covering it with fine graphite powder—and the tablet is then hung, as the negative electrode, in an aqueous solution of a metal salt, copper sulfate, for example, while a metal plate, copper, for instance, is made the positive electrode. If a current is passed through this system, galvano-plastic copper precipitates on the tablet, hermetically sealing it and making it possible to heat it highly in an oil or air bath. After the reaction is over, the metal-coated paraffin plate is cooled, fastened in a vise and opened by filing, breaking off, or etching one corner. The advantage of this procedure may be characterized about as follows: (1) avoidance of the very disagreeable breaking of the vessels, that occurs so easily with sealed tubes; (2) possibility of allowing large quantities of materials to react at one time, since the tablets may be large; (3) the convenience of the four sided tablets, as any number of them may be heated above, or next to each other, in a bath; (4) the possibility of carrying out new chemical reactions (a) because of the complete exclusion of air from the reaction vessel; (b) by utilizing various types of contact actions of different enveloping metals at high temperature and high internal pressure.

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[5] Wolfson, Franz, *Ch. Zt.*, **33**, 1077 (1909).

AVOIDING EXCESSIVE PRESSURE AS WELL AS RISE OF PRESSURE IN SEALED TUBES

Excessive gas pressure may be avoided by not placing all of the material producing gas in the tube at one time. If bromine, for example, produces hydrogen bromide, one third of the total quantity necessary is added, the tube opened after the reaction is complete, the second third added, the tube resealed, and so on. If the evolution of gas is due to heating to very high temperatures, the tube is first heated to, say 200° only, the pressure relieved after cooling, the tube resealed and then heated to the requisite higher temperature. If, on the contrary, the pressure in the tube does not rise high enough, and it is desired to have a higher pressure during the heating without raising the temperature excessively, an indifferent, low boiling liquid like ether, acetone, or chloroform, is placed in the tube along with the materials which are to react. These will produce the necessary pressure at a comparatively low temperature.[6] To give some idea of this behavior a few figures for water, ether and chloroform are given (see table 4).

High pressures may be produced at much lower temperatures if gases such as carbon dioxide, are pumped into metal vessels at ordinary temperatures, and then heated. This procedure is due to Werner and Kunz[7] who, in their attempts to have carbon dioxide act under pressure upon sodium phenanthrolate, met the same difficulties which had always been encountered in the laboratory with such problems. The addition of carbon dioxide, for example, in the form of snow is a very uncertain operation. If calculated quantities are used, loss by volatilization occurs, while an excess increases the danger because of the rising pressure with rise in temperature. Furthermore, ice always condenses on the solid carbon dioxide. Finally, they constructed the following apparatus which undoubtedly will be useful in many other instances, in which gases under high pressure are to act upon solid or liquid materials at desired temperatures (fig. 87).

TABLE 4

Pressure effects of heating water, ether and chloroform

PRESSURE IN ATMOSPHERES	WATER	ETHER	CHLOROFORM
2	at 121°	at 56°	at 83°
4	144	80	109
6	159	96	127
8	171	109	141
10	180	119	152

An annealed steel flask *A*, 300 cc. capacity, whose bottom is raised about 1.5 cm. into the jacket, has a thread on its neck like those on carbon dioxide cylinders. The jacket rising above the bottom is cut out at three places, so that the flask stands on three feet. A cock is screwed into the neck and a light copper tube carrying a manometer leads to the valve of a gas bomb *B*. The flask is filled with carbon dioxide by first connecting the vessels, opening the valve in the flask and finally slowly opening that of the bomb.

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[6] As reaction velocities depend on the partial pressures of the reactants and as these are not altered by the presence of an inert gas, it is hard to see the advantage of such addition.—E. E. R.

[7] Werner, A., and Kunz, J., *Ber.*, **35**, 4421 (1902).

The manometer indicates the rise of pressure and as soon as this is as high as is desired—20 atmospheres, for example—the valve of the bomb is closed. The pointer of the manometer indicates whether the joints are tight; if it remains fixed, the flask is closed and the filling has been completed. The maximum pressure attainable when working with carbon dioxide is 50 atmospheres, which is that of liquid carbon dioxide at room temperature.

If the flask filled with carbon dioxide is heated in the oil bath *C* in which it is immersed up to the valve—the slightest leak between the flask and the valve is betrayed by bubbles in the oil—the pressure will rise and its final value may be calculated from the initial pressure. In their experiments the initial pressure was 20 atmospheres at 15°, consequently, the final pressure at 250° was 36.4 atmospheres. This final pressure was never attained because a part of the carbon dioxide was consumed during the process.

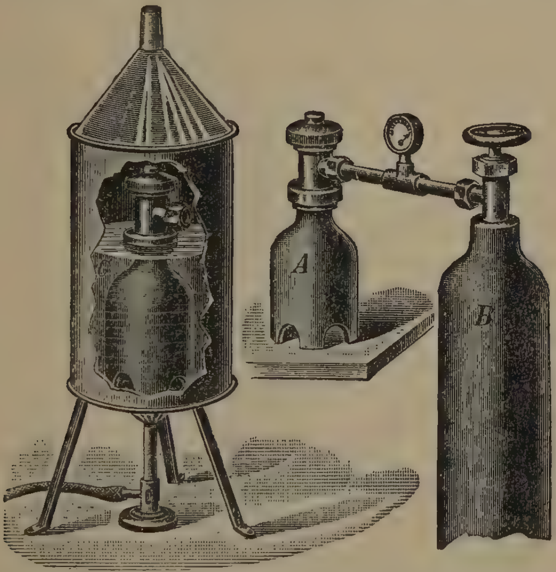

FIG. 87. WORKING WITH CARBON DIOXIDE UNDER PRESSURE (WERNER AND KUNZ)

While studying the hydrolysis of organic materials, Pfyl required an apparatus in which it was possible to take account of temperature, choice of gas atmosphere, pressure, and also permit exact quantitative manipulation. The pressure flasks, cylinders, autoclaves, etc., known at that time met these requirements only partially. He devised a pressure cylinder suited to his purposes, which has given excellent service for several years. It is described here (fig. 88) because it should be of general use for investigations requiring working under pressure, particularly for quantitative hydrolyses with carbon dioxide at desired measurable pressures. *C* is a thick walled phosphor-bronze cylinder about 31 cm. long, 2 to 3 cm. internal, and 4 cm. external diameter. It is threaded on the top and the extension *A* can be screwed on and made air tight by means of a lead seal. Inside the extension there is a conical valve which permits gases under pressure to enter, but not to escape. A manometer is screwed in tightly on the side of the extension. Threads are cut in the top, and a cap *H* may be used to close this air tight with the aid of a lead gasket. A glass tube *G*, which serves to hold the substance, fits into the cylinder *C*. The tube is constricted at the top and carries a mark which aids in regulating the volume of the liquids. The desired pressure, which may be read from the manometer, is attained by connecting the thread of the extension with the carbon dioxide, nitrogen or oxygen cylinder, etc., and then allowing somewhat more gas than is necessary to enter. The conical valve alone does not close the apparatus perfectly. After waiting till the escape of the gas from the valve has produced the desired pressure, the apparatus is sealed hermetically by the cap *H*. To release the pressure, the cap is unscrewed or drawn on again over a stud placed beneath it. If an atmosphere of a particular gas is desired, the gas is first passed through the cylinder and then through the extension while it is being screwed on. For experiments up to 160°, it is best to suspend the cylinder in a glycerol bath, and the temperature is regulated by means of a stirrer and thermo-regulator. Suitable air baths were used for higher temperatures. For ordinary purposes, the apparatus has been tested up to 80 atmospheres and found perfectly tight. It is provided with a manometer reading to 50 atmospheres.

This technique is entirely different from working with liquefied gases which are put into open glass tubes which are then sealed. This procedure is treated under a separate heading.

DETERMINATION OF THE PRESSURE IN SEALED TUBES

The pressure in sealed glass tubes may be determined by the procedure of Reychler[8] (fig. 89). A thin glass tube about 40 cm. long has one end silvered inside for a length of 4 to 5 cm., then is bent in the middle, and filled with mercury to a certain height. After the tube is sealed at the silvered end, the mercury in the open end is covered with a protective layer of hydrocarbon. After measuring the length L of the air column AB, reading the temperature t and the air pressure P, the apparatus is pushed into the tube containing the materials to be worked with, and the tube sealed. The pressure developed in the tube forces the mercury to rise in the closed arm of the pressure gauge, dissolving the silver to a point C. After the operation, the pressure gauge is removed, and the distance $AC = L'$ is measured. This corresponds to the maximum pressure. At the temperature t' of the heating bath, the pressure in the tube has risen to P millimeters of mercury. The vapor tension of the mercury is taken as h'. The pressure is calculated by the formula:

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[8] Reychler, A., *Ber.*, **20**, 2461 (1887).

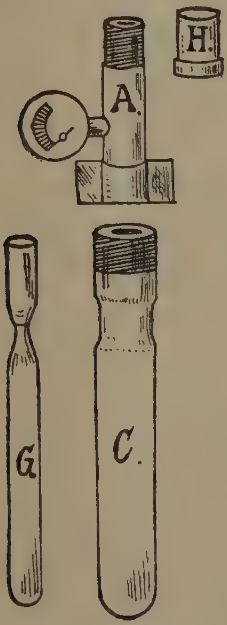

FIG. 88. PRESSURE CYLINDER (PFYL)

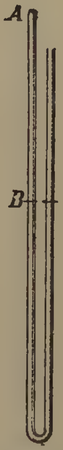

FIG. 89. MANOMETER FOR SEALED TUBES (REYCHLER)

$$P' = \frac{L \cdot P \cdot (1 + \alpha t')}{L' (1 + \alpha t)} + h' \text{ mm. mercury.}$$

This method of determining pressure is only approximate since the length L' cannot always be read accurately. The silvering should be done very carefully and the apparatus set up vertically or nearly so. Comparative experiments in autoclaves with manometers have checked the pressures determined with this apparatus.

EXPERIMENTS WITH SMALL PORTIONS

The Drechsel method of carrying out small scale experiments in a sealed tube, may be highly recommended.[9] Experiments in sealed tubes of the ordinary dimensions require much material, which frequently is lost by explosion. Preliminary experiments with a few milligrams may be made by using an ordinary glass tube, 3 to 4 mm. in diameter and 1 mm. wall, as the sealed tube. The tubes are sealed at one end, charged when cool, and then drawn out to a very long, thin-walled capillary. The final length of the tube itself should not be more than 5 to 6 cm.; but the capillary should have a length of 10 to 15 cm. The tube is placed in a long, wide test tube and fastened in place by a loosely fitting cork stopper, cut through lengthwise, the lower end of the tube being about 1 to 1.5 cm. from the bottom of the test tube. Enough of a liquid of the desired boiling point is put in the test tube so that the sealed tube is about half covered. This is heated to boiling, the flame being regulated so that the entire small tube and a portion of its capillary, are surrounded by the vapors which, however, must not reach the cork. The whole apparatus should be put in a hood and the window lowered. Since experience has shown that such glass tubing can withstand high pressures, there is little danger of explosions; but if one should occur the results are insignificant, even when heating in sulphur vapor, for example. If the experimenter has learned something as to the course of the reaction by such small scale preliminary experiments, it is much easier for him to arrange for more extensive ones.

THE OPENING OF TUBES

Tubes in which reactions have occurred should always be opened cautiously. They must be perfectly cold. If easily volatile materials, such as methyl chloride may have been formed, it is well to cool the tube with ice before opening it. If the gases formed need only be considered in connection with the operator's personal safety, the whole tube, with the exception of the tip, is wrapped in a cloth fastened in a clamp and the tip heated in a flame.[10] The experimenter should then step back a few paces. As soon as the glass softens in the flame, the gases blow the tube open and escape without carrying with them any of the contents of the tube, unless the pressure is excessive. If, however, there is danger that a part of the contents of the tube may be spattered out by too great pressure, a flask with a wide neck should be fastened opposite the tip, so that anything ejected is caught in it.

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[9] Drechsel, E., *J. pr. Ch.*, [2], **27**, 422 (1883).

Staedel[11] states that tubes containing much hydrobromic acid, a common case, are best opened by filing the tips under water. The tubes are thus emptied through a very fine opening, with no loss whatsoever, and he has never had an accident though he has repeated this operation many times. After the gases have escaped, part of the tip is broken off so that the contents of the tube may be removed. However, it is always wise to wear a safety mask while opening tubes. Recently, tubes containing gases under high pressure have been cooled in liquid air before opening them. Thus, in preparing acetobromglucoses and analogous compounds, Fischer and Armstrong[12] took 10 to 15 cc. of hydrogen bromide of the highest possible purity, dried with phosphorus pentoxide, to each 10 grams of acetyl compound, and sealed them in a tube cooled with liquid air. After heating, the tube was again cooled with liquid air and then opened.

The writer knows of only one instance of tubes being opened while warm. Einhorn[13] reported heating 10 grams of nitrocinnamic acid with 100 grams of glacial acetic acid saturated at 0° with hydrogen bromide, and shaking the tube in a bath of warm water until the acid had dissolved. He opened the warm tube immediately so that the excess of hydrogen bromide could not exert an injurious effect upon the addition-product formed.

Nef,[14] in his very important studies of prussic acid, had to work frequently with this acid in sealed tubes and was compelled to protect himself against its toxic effect in all contingencies, including the accidental explosion of a tube while it was being heated in a furnace. His experiences in this field are given here because they indicate how it is possible to work safely with sealed tubes containing such dangerous materials. A perfectly air tight protection for the eyes may be made from clear goggles, with the aid of sheet rubber and shellac. He also had a breathing apparatus constructed which was fitted with valves and long tubes. This was fitted around the head and fastened around the body by a belt so that the wearer could easily move and work. When wearing this apparatus it was possible to safely enter a room in which sealed tubes containing prussic acid were likely to explode suddenly. The apparatus may also be used with advantage when working with bromine, phosgene, cyanogen chloride and other materials which attack the lungs. Nef and his assistants were thus protected from the very disagreeable, chronic physiological effects of prussic acid.[15]

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[10] A safer procedure is not to remove the tube before opening it (since an accidental jar may cause it to explode in the operator's hands), but to apply the flame to the tip, which should protrude 1 to 2 cm. outside the bomb-furnace. Only when the pressure has been relieved is it safe to handle the tube in any way.—H. T. C.

[11] Staedel, W., *Ann.*, **195**, 190 (1879).

[12] Fischer, Emil, and Armstrong, E. F., *Ber.*, **35**, 833 (1902).

[13] Einhorn, Alfred, *Ber.*, **16**, 2208 (1883).

[14] Nef, J. U., *Ann.*, **287**, 358 (1895).

COLLECTION OF EVOLVED GASES

If gases which are to be studied are evolved when a sealed tube is opened, they are collected in a gasometer of the proper size, and later led through absorption apparatus charged with ammoniacal silver solution, dilute hydrochloric acid, ferrous sulfate solution, bromine under water, potassium hydroxide solution, baryta water, or basic lead acetate solution. Acetylene, allylene, etc., produce, with ammoniacal silver solution, precipitates which must be dried in a vacuum and are then very explosive. Hydrochloric acid combines with ammonia and volatile bases. Bromine is dissolved by dilute, cold potassium hydroxide. If an oil still remains, it is an addition-product of bromine and unsaturated compounds. Acids combine with potassium hydroxide and baryta water, which may be replaced by ammoniacal barium chloride solution. It is worthy of note that Dupré and Hake[16] found that a 2 per cent solution of basic lead acetate still showed a turbidity with carbonic acid, when baryta water had already failed, which is the reason for including this reagent here. Ferrous sulfate solution absorbs nitric oxide. Any gases left unabsorbed can be determined with certainty by a quantitative analysis only, but in general, their composition may be deduced from the reaction equation, and their identity established by qualitative tests.

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[15] Suitable masks protective against all types of gas are obtainable on the market.—H. T. C.

[16] Dupré, A., and Hake, H. W., *J. Ch. Soc.*, **35**, 163 (1879).

Carius[17] recommends catching the gases escaping from tubes under high pressure, as follows: a rubber tube is led above the middle of a measuring tube filled with water. The lower end of the rubber tube is fastened tightly to a bent, short, wide glass tube, whose second arm extends upward and carries a short piece of rubber tubing into which the point of the sealed tube is tightly pushed below the confining liquid, so that the capillary end of the tube reaches as for as the bent glass tube. The tip of the tube is now carefully broken off, and part of the gases escape very rapidly, and almost all of the liquid is forced out with them. Salkowski[18] has given exact directions for quantitatively collecting ammonia from sealed tubes (for example, the urea determinations by Bunsen's method.)

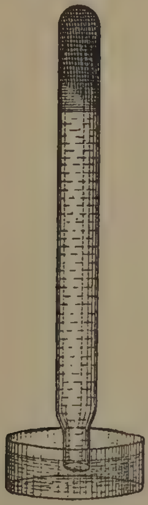

FIG. 90. EMPTYING A SEALED TUBE (LASSAR-COHN)

EMPTYING THE TUBES

If the content of a tube is solid after it has been cooled, but is soluble to some extent in a solvent, it is best removed without injuring the tube, by filling the latter with the solvent, inverting and then standing it in a beaker with the opening under the solvent (fig. 90). The action of the solvent on the solid forms a heavy solution which sinks, while a less concentrated solution is continuously reaching the solid, dissolving it in a short time.

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[17] Carius, L., *Ann.*, **169**, 318 (1873).

[18] Salkowski, E., *Z. physiol. ch.*, **4**, 64 (1880).

HEATING TUBES

Glass sealed tubes are heated in iron pipes lying in tube furnaces. A thin wire is wound around each of them as shown in figure 85, so that they may be withdrawn from the protecting pipes after the reaction is over, without danger of subsequent breaking.

According to Babo,[19] a tube furnace should meet the following requirements:

(1) It must permit the heating of several tubes of the usual size to temperatures approaching the boiling point of mercury, and the individual tubes must be heated as uniformly as possible.

(2) It must be possible to measure the temperatures used and the apparatus should be so arranged that a certain maximum cannot be exceeded.

(3) If one tube explodes, the others should be affected as little as possible and there should be no danger to the experimenter.

(4) The gas consumption should be as small as possible and the temperature should not vary appreciably through the fluctuations of the gas pressure, which always occur. Therefore, it is well to insert gas pressure regulators. The device of Giroud, already described under the heading "Baths," has proved very valuable for this purpose, because of its simple construction and its sturdiness.

These furnaces should be set up under hoods, so that the vapors liberated by the explosion of a sealed tube will produce no unpleasant consequences.

Because of the great advantage offered by mechanical agitation in many chemical operations, Emil Fischer,[20] who recognized the necessity of constant mixing during reactions carried out in sealed tubes, was led to devised a tube furnace permitting this. The following findings of Fischer[21] indicate some of the effects of shaking. When he heated 3 grams of amorphous phosphorus with 10 cc. of fuming hydriodic acid, specific gravity 1.96, in a sealed tube for twelve hours at 100°, the phosphorus disappeared entirely, and after cooling, about 8 grams of beautifully crystalline phosphonium iodide separated. Since the liquid contained phosphorous acid as well as phosphoric acid, the course of the reaction had to be considered from the standpoint of both the equations:

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[19] Babo, L. von, *Ber.*, **13**, 1219 (1880).

[20] Fischer, Emil, *Ber.*, **30**, 1485 (1897).

[21] Fischer, Emil, and Leuchs, Hermann, *Ber.*, **35**, 3793 (1902).

$$2\ P + 3\ H_2O = H_3PO_3 + PH_3$$
$$8\ P + 12\ H_2O = 3\ H_3PO_4 + 5\ PH_3$$

When the experiment was repeated under the same conditions, except that the tube was shaken continuously, the phosphorus was completely consumed after only four hours.

Following Fischer's model, Thoms[22] designed the shaking apparatus illustrated in figure 91. The hot air motor *A* ($\frac{1}{40}$ horse power) of the Henrici type shakes the furnace *B*. The temperature can be easily raised to 300° by small flames rising from a heating tube, and may be kept constant within 1 to 2° by means of a regulator. The steel removable tubes, are held in place by screws. The glass tubes are held in them during the shaking, by spirals of steel wire placed at both ends. This device does not permit observation of the contents of the tube while it is being heated. Though this is ordinarily dispensed with it would be very convenient. If necessary, such observation can be made according to Junghahn,[23] by using the furnace shown in figure 92, which, however, was designed only for the heating of a tube. The inner, strong-walled copper tube, in which the sealed glass tube is placed, is fastened firmly by screws to the front and back walls of the furnace. The right rear end of the copper tube is provided with a strong bayonet catch. The sealed tube which has an external diameter of 18 to 19 mm. and an approximate length of 40 cm., is placed in the carrying device shown in the upper illustration. This device, provided with an elastic metal clamp, is then put into the copper tube and fastened in the furnace by means of the bayonet catch. When desired, the contents of the tube may be observed by pushing it out of the rear end of the tube to a distance of 15 to 18 cm. using the wooden handle. A thick walled glass tube fastened on the rear end of the furnace forms an extension of the copper tube, and is a guide in pushing the device in and out. It requires only a very slight turning of the handle to open or close the bayonet catch. Should the tube accidentally explode while lying in the copper tube, there is absolutely no danger, since the explosion occurs as it would in any other tube furnace. Since it is possible that the tube may explode just at the instant it has been withdrawn for observation, an additional safety device is necessary for the operator. This consists of a safety shield made of strong sheet iron, and shown by dotted lines in the illustration. It surrounds the rear end of the furnace, and has only a small slit for the carrying device, and two small windows at the side which are closed with very heavy glass panes. A small slit burner is placed

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[22] Thoms, H., *Ber.*, **36**, 3958 (1903).

[23] Junghahn, A., *Ch. Zt.*, **26**, 1176 (1902).

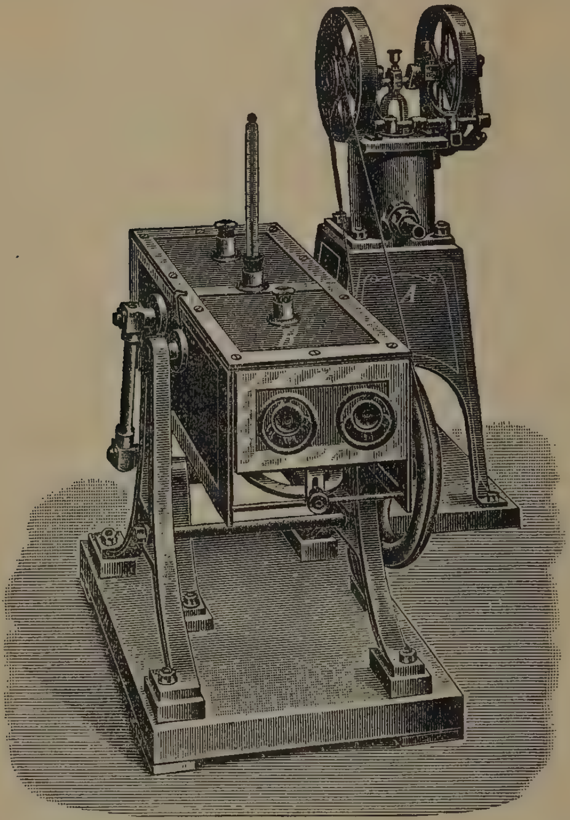

FIG. 91. BOMB FURNACE WITH SHAKING MECHANISM (THOMS)

at the proper height just behind the outer glass tube to provide illumination for the observation within the safety chamber. The furnace is not set horizontally, but is mounted at an angle so that the contents of the sealed tube will collect in the lower end.

The furnace is also provided with a simple and convenient device for safely opening the tube in the furnace itself. Taking a sealed tube, which carries considerable pressure, out of a furnace, is always attended by some danger. This is avoided by the following arrangement: The hollow metal core of the carrying device contains a strong iron wire having a smaller handle. Using this, it is possible to push the sealed tube, after the reaction is over, so far out of the clamp, that the tip extends out of the forward portion of the copper tube and may be safely opened by a flame. This new bomb furnace served Junghahn exceedingly well, especially in a study of α-*m*-xylidine-5-sulfonic acid,[24] *i.e.*, for the cleavage of the sulfonic acid with hydrochloric acid at 150 to 155°; and also in the preparation of the ethoxy derivative, by heating the diazo compound with absolute alcohol, etc. In the last case, he could observe exactly how the diazo compound completely dissolved in the course of 15 minutes at 100 to 125°, with evolution of gas (nitrogen). Only under these conditions, was the ethoxy derivative produced smoothly; longer or higher heating led to decomposition.

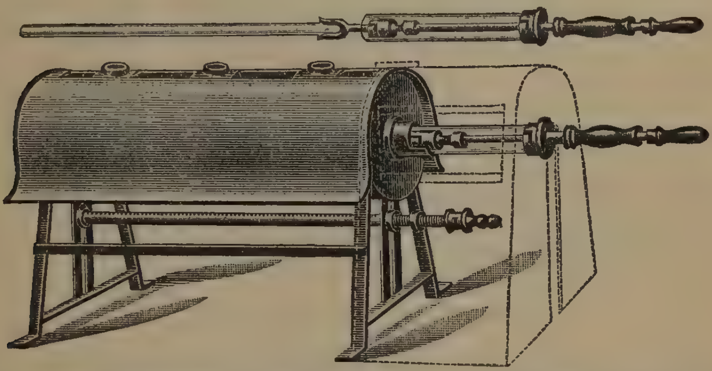

FIG. 92. BOMB FURNACE FOR THE OBSERVATION OF HEATED SEALED TUBES (JUNGHAHN)

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[24] Junghahn, A., *Ber.*, **35**, 3747 (1902).

WORKING WITH CHLORINE, HYDROGEN IODIDE AND AMMONIA IN SEALED TUBES; RESULTS OF WORKING WITH AMMONIA

A problem often encountered, is the liberation of chlorine and ammonia in sealed tubes. Chlorine may be generated as follows: The material in the sealed tube is covered with hydrochloric acid and a wad of glass wool placed over it. Potassium bichromate, potassium chlorate, or manganese dioxide[25] is placed on this. After the tube is sealed and placed in the furnace, the chlorine begins to form. If a weighed quantity of potassium bichromate is taken, it is easy to evolve chlorine in stoichiometric quantities. Potassium chlorate is not so good, because it produces chlorine dioxide.

Lagermarck[26] wished dry hydrogen iodide to react in a sealed tube on vinyl bromide to secure a good yield of ethylidene bromoiodide. To do this, he placed a weighed quantity of phosphorous iodide, PI_3, in a sealed tube, along with a bulb containing just enough water to decompose the phosphorous iodide. After thus charging and sealing the tube, it was placed in a freezing mixture. The water froze and burst the bulb, and when removed from the freezing mixture, the melting ice reacted with the PI_3 forming dry hydrogen iodide and phosphorous acid:

$$PI_3 + 3\ H_2O = 3\ HI + H_3PO_3$$

For about twenty-five years there has been considerable interest in the development of the use of ammonia in sealed tubes. Up to 1880 it was assumed that ammonia would not replace the hydroxyl groups of either the aliphatic or the aromatic series, even under pressure. Methyl alcohol, CH_3OH does not react with it to produce methylamine, CH_3NH_2, nor does phenol, form aniline, $C_6H_5NH_2$. About that time, it was found that this behavior was different as soon as substituted phenols were used, or if a multiple benzene nucleus was present in the hydroxyl compound. In such cases, the ammonia easily reacts with the hydroxyl group, and thus β-naphthylamine, $C_{10}H_7NH_2$, may be prepared from β-naphthol, $C_{10}H_7OH$, by heating it to about 160° with ammonia. The procedure is described below.

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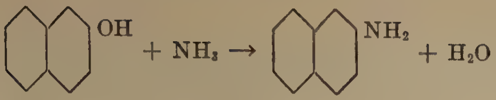
[25] Zincke, Th., and Campbell, C., *Ann.*, **255**, 370 (1889).

[26] Lagermarck, H., *Ber.*, **7**, 912 (1874).



Ammonia is introduced into the tube by previously absorbing it by zinc chloride, zinc bromide, or calcium chloride. The gaseous ammonia required for the preparation of these compounds is best generated, as is all gasous ammonia to be used in the laboratory, according to Neumann,[27] by dropping ammonia water onto solid potassium hydroxide. A vigorous current of the gas may be generated for ten hours from 200 grams. This method is not expensive, because the solution remaining after the generation of the gas may be freed of the ammonia dissolved in it by warming, and can then be used as aqueous potassium hydroxide. It should be noted that the ammonium hydroxide must be added very slowly, particularly at first.

Benz[28] states that if dry ammonia gas is passed over anhydrous calcium chloride, even in compact form, it is generously absorbed by it with great evolution of heat, and a white powder is formed. When powdered calcium chloride was used there was still slight absorption after twelve hours, and the preparation contains 47 per cent of ammonia.

Zinc diammino chloride is obtained according to Merz and Müller,[29] by passing dry ammonia gas through molten zinc chloride in a retort. The gas is rapidly absorbed with rise of temperature. After the saturation is completed, the product is cooled in a current of the gas. Thus prepared, it forms a solid transparent mass, having the composition $ZnCl_2 \cdot 2NH_3$, which is not deliquescent in the air. It is well to add ammonium chloride because this opposes the formation of the zinc oxychloride by the partial decomposition of the normal chloride. Zinc diammino-bromide is prepared in the same way, but is hygroscopic. Its composition corresponds to the formula, $ZnBr_2 \cdot 2NH_3$.

The temperature to be used, and the length of heating when using these preparations, may be learned from the following example:[30]

[27] Neumann, G., *J. pr. Ch.*, [2], **37**, 343 (1888).

[28] Benz, G., *Ber.*, **16**, 8 (1883).

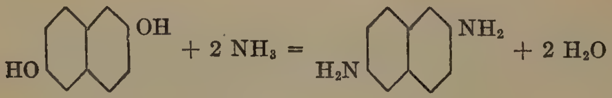
[29] Merz, V., and Müller, P., *Ber.*, **19**, 2902 (1886).

[30] Müller, P., *Ber.*, **20**, 1039 (1887).

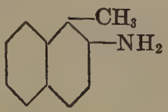
A mixture of 1 part xylenol $C_6H_3(CH_3)_2OH$, and 3 parts zinc ammino-bromide, and 1 part ammonium bromide heated to 340°, for 40 hours, gave a 25 per cent yield of xylidine, $C_6H_3(CH_3)_2NH_2$. Seyewitz[31] heated resorcin, $C_6H_4(OH)_2$, for 3 hours, in a sealed tube at 300°, with 4 parts calcium ammino-chloride, and converted 60 per cent of the resorcin to meta phenylene diamine, $C_6H_4(NH_2)_2$. These results differ somewhat from those obtained by the technical procedures to be discussed later.

Dienel obtained a 25 per cent yield of α-anthramine by heating α-anthrol with acetamide in a Pfungst autoclave. However, Pisovschi[32] raised this to 70 to 80 per cent, by heating α-anthrol in a sealed tube for one day, at 200 to 220°, with 3 to 4 times its weight of calcium ammino chloride. He put only 3 to 4 grams of α-anthrol in one tube. The contents of the tube were extracted by boiling with 0.5 per cent hydrochloric acid, and the anthramine precipitated by ammonia.

Jacchia[33] heated 2,6-dihydroxynaphthalene with finely ground calcium ammino-chloride for seven hours in a sealed tube at 270°. When the hard baked mass was put into hot water, the calcium chloride dissolved, leaving behind most of the difficulty soluble diaminonaphthalene.



Fries[34] heated 1 part of methyl-naphthol with 4 parts calcium ammino-chloride in a tube for eight hours to about 270° to obtain 1-methyl-2-naphthylamine,



The contents of the tube were washed out with water when cooled, and the amine extracted by ether. When Benz[35] heated β-naphthol for two hours at 200° with 2 to 3 times its weight of calcium ammino-chloride, naphthylamine amounting to 25 to 26 per cent of the weight of the naphthol was formed; after eight hours, 45 per cent; after thirty-two hours, 70 per cent. On heating to 240 to 250°, the yield after eight hours, was 55 per cent. The maximum yield, 80 per cent of the weight of the naphthol used, was obtained by heating 1 part naphthol with 4 parts calcium ammino-chloride for two hours, at 230 to 250°; and then for six hours at 270 to 280°.

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[31] Seyewitz, A., *C. r.*, **109**, 814 (1889).

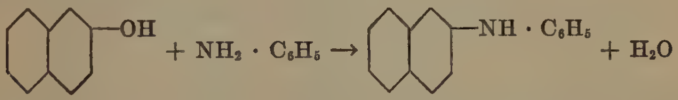
[32] Pisovschi, Ilie J., *Ber.*, **41**, 1434 (1908).

[33] Jacchia, A., *Ann.*, **323**, 132 (1902).

[34] Fries, K., and Hübner, E., *Ber.*, **39**, 444 (1906).

[35] Benz, G., *Ber.*, **16**, 10 (1883).

An idea of the technical working of this process is apparent from the following: 10 kgm. β-naphthol, 4 kgm. sodium hydroxide and 4 kgm. ammonium chloride were heated at 160 to 170° for sixty to seventy hours.[36] About half the β-naphthol had then been converted, and the operation was interrupted. The unchanged naphthol, having acid properties, was dissolved out in sodium hydroxide, while the naphthylamine, a base, was extracted from the residue by hydrochloric acid. If the ammonia in this process was replaced by a substituted ammonia, such as aniline, $C_6H_5NH_2$, there was obtained from 6 kgm. β-naphthol, heated to 170 to 190°, with 5 kgm. of aniline hydrochloride for seven to nine hours, β-phenylnaphthylamine. After this period, there was no further formation of water and hydrochloric acid.



While phenol does not react with ammonia, resorcinol (di-hydroxybenzene) and also phloroglucinol,[37] (tri-hydroxybenzene) do react with it, but all the hydroxyl groups do not always react. Meta aminophenol may be obtained technically by heating 10 kgm. resorcinol[38] with 6 kgm. ammonium chloride and 30 kgm. 10 per cent aqueous ammonia at 200° for twelve hours. To isolate it from the liquid, the latter is acidified, the unchanged resorcinol extracted with ether, the acid neutralized with soda, and the solution then evaporated until, on cooling, the meta aminophenol separates. Substituted ammonias, in this case also, lead to substituted meta aminophenols.

Under corresponding conditions, ammonia in sealed tubes may exert remarkable effects also on nitro groups. Probably, however, several nitro groups or similar substituents must be on the same ring in order for one of them to be more mobile. The influence of several groups on one ring with respect to their mutually increased reactivity, a point of great importance, is encountered here for the first time.

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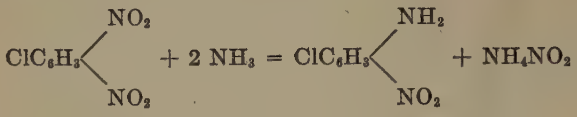
[36] Badische, A. S. F., German patent 14612 (1880); Fr. I, 411.

[37] Pollak, J., *Monatsh.*, **14**, 419 (1893).

[38] A. Leonhardt & Co., German patent 49060 (1888); Fr. II, 14.

Laubenheimer[39] observed that a solution of dinitro-chlorbenzene saturated with ammonia, reacts after four days standing in the following way:



$$\mathrm{ClC_6H_3}\left\langle\begin{matrix}\mathrm{NO_2}\\ \\ \mathrm{NO_2}\end{matrix}\right. + 2\,\mathrm{NH_3} = \mathrm{ClC_6H_3}\left\langle\begin{matrix}\mathrm{NH_2}\\ \\ \mathrm{NO_2}\end{matrix}\right. + \mathrm{NH_4NO_2}$$

To this should be added the fact, previously determined by Clemm,[40] that when dinitro-chlorbenzene is heated with strong ammonia in a sealed tube to 120°, not one nitro group, but the chlorine is replaced by the amino group:

$$\mathrm{C_6H_3(NO_2)_2Cl} + 2\,\mathrm{NH_3} = \mathrm{C_6H_3(NO_2)_2NH_2} + \mathrm{NH_4Cl}$$

Under proper conditions, such reactions may even proceed quantitatively. Thus Lobry de Bruyn[41] found that ortho nitraniline is obtained quantitatively, by heating ortho dinitrobenzene in a sealed tube at 100° for eight hours, with methyl alcoholic ammonia:

$$\mathrm{C_6H_4(NO_2)_2} + 2\,\mathrm{NH_3} = \mathrm{NO_2{\cdot}C_6H_4{\cdot}NH_2} + \mathrm{NH_4NO_2}$$

In 1893, he still believed this the best method of preparing ortho nitraniline, through obviously it was a very inconvenient one, because of the necessity for using the sealed tube. Shortly thereafter, the problem of preparing ortho nitraniline far more conveniently, was solved technically, by making use of the fact that simply boiling with sulfuric or hydrochloric acid is sufficient to remove a sulfonic group from aromatic bodies; sealed tubes being unnecessary. This method of removing sulfonic groups will be discussed later.

The behavior of dinitro-chlorobenzene toward ammonia in sealed tubes has just been discussed. In the same connection, the behavior of nitro-chlorobenzene, recently investigated, is very interesting. A quantitative yield of *p*-nitraniline is obtained by heating pure *p*-nitro-chlorobenzene to higher temperatures with an excess of ammonia.[42] This fact was known in 1904. In 1870, Englehard and Latschinoff[43] stated that this replacement was very incomplete at 130°. The conditions necessary for a quantitative yield were not investigated by them. These are as follows: the para nitro-chlorobenzene must be pure; the ammonia must be free from organic bases, especially pyridine, since the latter furthers the formation of brown by-products hard to remove, (many metals such as iron, lead and copper have a similar influence and consequently only enameled metal autoclaves may be used); large excess of ammonia must be used and the temperature raised to 165 to 170°; the addition of alcohol which increases the solubility of the *p*-nitro-chlorbenzene accelerates the replacement. For example, if 157.3 parts of *p*-nitro-chlorbenzene are heated for eighteen hours at 165 to 170° under pressure, with a quantity of 30 per cent aqueous ammonia equivalent to 18 mols, and filtered after cooling, the yield of para nitraniline is 98 per cent of the theory. It shows the correct melting point at once.

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[39] Laubenheimer, Aug., *Ber.*, **9**, 1826 (1876).

[40] Clemm, C., *J. pr. Ch.*, [2], **1**, 170 (1870).

[41] Lobry de Bruyn, C. A., *Ber.*, **26**, 267 (1893).

Since methyl alcohol at 0° dissolves 41.5 per cent, and at 28°, 17.4 per cent of ammonia gas, while ethyl alcohol at the same temperatures dissolves 24.5 per cent and 10.1 per cent respectively, the former solution especially is worthy of consideration for work in sealed tubes. Water at 0° takes up 52.5 per cent, and at 15°, 35 per cent of ammonia gas. Details concerning the addition of ammonia to unsaturated compounds will be given later when discussing the use of iron sealed tubes.

WORKING WITH LIQUEFIED GASES IN SEALED TUBES

Liquefied gases are now used much more commonly than formerly. There are two principal reasons for this: first, the easy preparation of liquid air, the best and comparatively cheapest cooling agent; and second, the general distribution of Dewar containers which reduce to a minimum the losses due to external heating. In addition to the liquefied gases such as sulfur dioxide, chlorine and ammonia, which have been used even in technical practice for a long time, anhydrous liquid hydrogen halides, hydrogen sulfide, phosphine, arsine, etc., are now commencing to be of importance. With their aid, new results are achieved in the organic field also, as shown for example, by the work of E. Fischer. His method of working with liquefied hydrogen chloride supplemented the general findings of Stock and B. Hoffmann. These two investigators,[44] after working with liquefied gases continuously for years, published their accumulated experiences in 1903 and took cognizance of the work of Moissan.[45]

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[42] Clayton Aniline Co., German patent 148749 (1902); Fr. VII, 66.

[43] Engelhardt, A., and Latschinoff, P., *Z. f. ch.*, **6**, 234 (1870).

Their experiments dealt chiefly with liquid ammonia, but their findings may be applied, *mutatis mutandis,* without difficulty, to other gases. They used either ordinary bending tubing or so called "double annealed" soft glass. Both varieties, scarcely attacked by the anhydrous gases mentioned withstand high pressures well, if some care is taken in their selection. Pieces with bubbles in the glass or with scratches on the surface should be rejected. Because of the high pressures usually prevailing, special care must be taken while sealing and cooling; the bottoms and capillaries must be absolutely uniform, and are best if not thicker than the rest of the tube. The walls of the tubes should be as thin as possible, thus diminishing considerably the danger of breakage while cooling. Tubes having walls 1.2 mm. thick and 10 mm. internal diameter held liquid ammonia at 100° (about 60 atmospheres pressure). For greater internal diameters, up to 20 mm., the thickness of the walls should be increased to 2 mm. If larger quantities of substances are to be worked up longer tubes should be used; diameters more than 20 mm. are advisable only if the tubes are not to be heated.

An alcohol bath cooled with liquid air is used as a cooling agent when condensing the gases. A Dewar cylinder is used as container, and its edge is protected from contact with liquid air, and from breakage, by a rubber cap. The liquid air is forced over, out of the container, by a rubber bulb. The gas to be condensed is led in through a long tube, whose lower end is drawn out to a capillary extending to the bottom of the tube to be sealed. The liquefaction is most complete if the capillary dips into some of the gas previously condensed. The addition of more liquid air to the alcohol bath is required about every hour, if the gas current is rapid. If it becomes necessary to interrupt the liquefaction, say over night, the alcohol is frozen by a larger quantity of liquid air, covered with liquid air, and the upper opening of the Dewar cylinder is closed around the tube with cotton wool. In this way liquid ammonia may be kept for twenty-four hours. The charged tube is easily sealed if the capillary is drawn out with the right hand, while the tube, together with the Dewar flask is held by the left hand.

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[44] Stock, A., and Hoffmann, B., *Ber.*, **36**, 895 (1903).

[45] Moissan, H., *C. r.*, **133**, 768 (1901).

Emil Fischer[46] pointed out, that if, for example, materials are placed in sealed tubes, in which they are to be treated with ammonia which has been dried by passage over lime, and which later is to be frozen in the tube, care must be taken that no moisture from the flame gases is carried into the tube when sealing it.

If the contents of the tube are not uniform, it is usually well to shake it. Glass beads and shot added for this purpose give good service. If, when cooled, the walls of a tube that has been heated are covered with material which it is desired to have within the liquefied gases, assuming that these dissolve the substance, ether is poured on the upper part of the upright tube. The cold caused by its evaporation, causes some of the liquid to distil up and wash down the walls. If the material adhering to the walls is not soluble, it often helps to dip the tube in liquid air. The lowering of the temperature usually causes crusts of substance to break away from the walls of the tube.

The contents of the tube are solidified in liquid air before opening. The evaporation of the liquefied gases from the opened tube is often too violent, and may be retarded by placing the tube in a wide, empty cylinder. This may be replaced by a Dewar flask if it is desired that the evaporation be very slow, so as to produce crystals.

The simple sealed tubes previously discussed do not suffice in many cases, as for example, when isolating or purifying crystals which have separated in the tube. The filter tubes of the form *A* (fig. 93) may then be advantageously used. The central enlargement which contains dried cotton wool as filtering material, is chosen as small as possible and the constrictions on each side are extended to short necks over which rubber tubes may be drawn after the tube is opened. These filtering tubes may be used in many ways and give excellent service. It is possible to filter from one side of them to the other. A solid body, which has separated, may be isolated and washed by immersing the lower end containing the solution in warm water, while keeping the upper end cold with a lead cooling coil, or, with a cooling mixture placed in a wide cylinder. In this way, pure solvent will distil through the cotton wool, wash out the solid and be drawn down again by cooling the lower half. This process may be repeated as often as desired and may also serve to purify by recrystallization materials slightly soluble in the liquefied gases. These precipitate in the lower portion during the repeated distillation and return of the liquefied gases.

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[46] Fischer, Emil, and Zach, Karl, *Ber.*, **44**, 133 (1911).

If a solid is to react with the liquefied gas in the filtering tube, there are four possibilities: (1) The material may be placed in the tube before the liquefaction; (2) it may be added to the liquefied gas; (3) it may be shaken onto the frozen gas; (4) it may be shaken onto the cotton wool in the upper chamber.

The first procedure is often not advisable because liquefying the gas over the substance causes the latter to adhere firmly to the bottom and masses it together, so that the reaction does not go to completion. The second method has the advantage that the course of a reaction may be followed in an open tube between the melting and boiling point of the gas in question and any gas generated may be allowed to escape before sealing the tube. The procedure is difficult or is entirely useless with substances which react as soon as they are added to the tube with the vapors of the liquefied gas in such a way that the necks of the tube are clogged. The third procedure is the most common, unless the reaction occurring is too violent and is accompanied by evolution of considerable heat. In this event, the material is first allowed to remain in contact with the vapors of the gas for some time, as is the case when the fourth method is used.

If a dissolved material is to react with a second one, one of the materials is treated by methods 1 to 3, and the other one by 4, and after sealing the tube, the first solution is run into the second by inverting the tube, or the second is dissolved by distilling up the solvent by the procedure described above.

Another modification of the filtering tubes (form *B*, fig. 93), will be described. By the use of a reflux condenser this effects a continuous washing or extraction, by the liquefied gases. In this, the solvent in the lower part is brought to a boil by immersion in warm water, or by means of a lead heating coil. The vapors pass through the inner glass tube, about 4 mm. wide, which is cut off at an angle at the bottom, into the upper part and are there condensed on the walls of the tube which is cooled by a lead coil. They then flow through the material to be extracted, through the cotton wool below it, and return to the lower part of the tube. The cotton filter rests on a slight constriction of the outer tube and is held in place by a slight enlargement of the inner one.

All the manipulations described are carried out under hoods and behind glass panes 60 cm. wide and 90 cm. high and at least 7 mm. thick. Stout leather gloves with clasps afford sufficient protection to the hands, even though a tube explodes while being held. When holding a filled tube the hand should not be placed over the tip, because this has the greatest impact during the explosion and usually forms the most dangerous missile. If it should be necessary to remove a tube filled with liquid gas from behind the protecting panes, goggles and wire gauze masks should be worn.

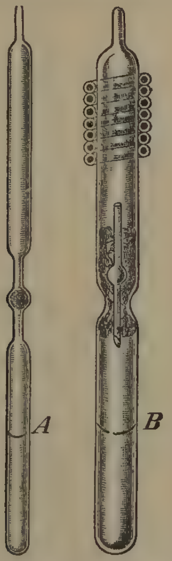

Fig. 93. Sealed Tubes for Use in Working with Liquefied Gases (Stock and Hoffmann)

E. Fischer and Armstrong[47] worked in the following way with hydrogen chloride liquefied by cooling. The material to be treated with this liquid is placed in a glass sealing tube and the upper part of the tube greatly constricted in the blast lamp to facilitate the subsequent sealing. Care should be taken while doing this to prevent water vapor from the blast flame from entering the tube. After the tube is placed in liquid air, a rather rapid current of hydrogen chloride gas, dried with concentrated sulfuric acid, is passed through the narrow neck, using a long but not too narrow capillary tube. If the capillary is too narrow, or if it extends too far down, it may easily clog when the gas freezes. At the low temperature the hydrogen chloride solidifies immediately and deposits on the cold walls of the tube. If care is taken that only the lower part of the tube is surrounded by liquid air at first, the quantity of hydrogen chloride may be judged rather closely. When it seems sufficient, the capillary tube is removed, and the tube is sealed off, with a small flame, at the constriction. It is now kept at room temperature, 15 to 20 hours, for example, cooled again in liquid air, the tip opened, and the tube placed in a quiet spot. Tubes made of poor quality of glass often explode while being opened, and the Dewar flask containing the liquid air may be ruined. Slimmer[48] found that even good tubes are damaged if cooled too suddenly by being dipped directly into liquid air. He recommends that the tube be placed in a wide, empty test tube which in turn is placed in the liquid air. The outer tube then acts as a protecting jacket and the sealed tube is cooled so slowly that there is no danger of its breaking. Nevertheless, it is always advisable that even here the experimenter wear heavy gloves and protect his head by an iron fencing mask, and his eyes with goggles. The contents of the tube are heated so gradually by the outer air that the hydrogen chloride evaporates, boiling gently. Any strong heating by water or by grasping the tube, should be avoided because excessive foaming is sure to follow.

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[47] Fischer, E., and Armstrong, E. F., *Ber.*, **34**, 2890 (1901).

OBVIATING THE USE OF SEALED TUBES

Removal of sulfonic groups, saponification of phenolic ethers in open vessels

Attempts will always be made to avoid using sealed tubes because of their great inconvenience. It is a source of pleasure to know that this has been done with respect to several group reactions. It was incorrectly assumed that the removal of sulfonic groups by means of hydrochloric or sulfuric acid from those aromatic sulfonic acids which were particularly suited for this reaction, could only be accomplished by heating with hydrochloric acid in a sealed tube. The interest in this reaction is ever recurring, and since there will be no other opportunity for discussing it, it will be dealt with here.

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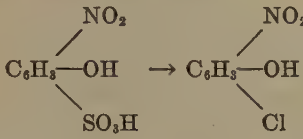
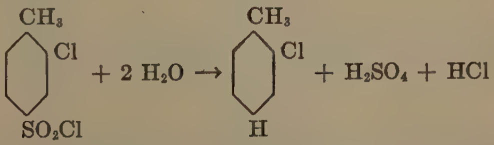
[48] Slimmer, M. (included in article by Fischer, E., and Armstrong, E.), *Ber.*, **35**, 835 (1902).

The earliest observation which indicated that a sealed tube was not necessary was, for many years, not applied in this sense. Schmitt and Glutz,[49] as early as 1869, showed that a sulfonic group could be split off by boiling with hydrochloric acid in an open vessel. They found that nitrochlorphenol is produced by passing chlorine into a solution of sodium nitrophenol-sulfonate:



In this case, the hydrochloric acid formed by introduction of the chlorine, sufficed to split off the sulfonic acid. The following facts may be stated in addition. *p*-Toluene-sulfone-chloride is obtained, as a troublesome by-product, in the preparation of saccharin from *o*-toluene sulfone-chloride. It is easily converted into ortho-*o*-chlor-*p*-toluene sulfone chloride[50] by melting 85 parts of it with stirring, adding 2 parts antimony trichloride, and passing in dry chlorine[51] at 70 to 80°, till the increase in weight reaches 15.5 parts. If this acid chloride is boiled with 80 per cent sulfuric acid, the $-SO_2Cl$ group is changed to SO_3H, and this sulfonic acid group is split off. Consequently, *o*-chlor-toluene is the product of this reaction, carried out in an open vessel.



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[49] Schmitt, K., and Glutz, L., *Ber.*, **2**, 52 (1869); Crafts, J. M., *Ber.*, **34**, 1350 (1901).

[50] Paysan, W., *Ann.*, **221**, 210 (1883).

[51] Ges. f. Chem. Ind. in Basel, German patent 133000 (1901); Fr. VI, 53.

In this way, this troublesome by-product has been converted into a material which is valuable as a starting point for the preparation of many other compounds. Similar observations have gradually accumulated, making this method of splitting off sulfonic groups with hydrochloric acid in open vessels a very common one in both laboratory and technical practice.

Thus heating with mineral acids at ordinary temperature, splits off the sulfonic group from 4-nitro-diphenylamine-2-sulfonic acid,[52] and also from 4-amino-diphenylamine-2-sulfonic acid. The mixture of 1 part 4-nitro-diphenylamine-2-sulfonic acid (sodium salt) and 10 parts of sulfuric acid (40 per cent) is heated on a water bath. Solution soon occurs, and after two to three hours, the *p*-nitro-diphenylamine separates in beautiful crystals. Turner[53] found that, if a solution of *o*-nitraniline-sulfonic acid in 3 times its weight of 67 to 68 per cent sulfuric acid is boiled for thirty minutes after solution has occurred, ortho-nitraniline in satisfactory yield is obtained as a consequence of the removal of the sulfonic group.

Friedländer[54] found an entirely different method of splitting off sulfonic groups in open vessels, *i.e.*, the treatment of sulfonic acids with sodium amalgam. He used 4 per cent amalgam for the reduction and allowed it to react in the cold with a 2 to 4 per cent solution of the derivative in question; for the naphthol sulfonic acids a weakly acid solution was used. For naphthylamine sulfonic acids, on the other hand, which are only slightly soluble in water, the reaction had to take place in alkaline solution, and was advantageously accelerated by simultaneous introduction of carbonic acid, or by intermittent neutralization. Extension of this reaction to a considerable number of sulfonated naphthalene derivatives showed him that the sulfonic group is easily eliminated in this way and replaced by hydrogen only when in the α-position. The β-sulfonic group, depending on its position, was also occasionally eliminated after long warming with sodium amalgam, but side reactions frequently occurred, leading to replacement of amino groups by hydrogen or hydroxyl.

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[52] Aktien-Gesellschaft für Anilin Fabrikation, French patent 379949 (1907); *Ch. Zt. Rep.*, **31**, 650 (1907); see also Ullmann, F., German patent 193448 (1906), Fr. IX, 129; German patent 193351, Fr. IX, 133 (1906).

[53] Turner, C., *Ber.*, **25**, 985 (1892).

[54] Friedländer, P., and Lucht, Ph., *Ber.*, **26**, 3030 (1893).

Gattermann and Schulze,[55] when applying this method to an amino-naphthol sulfonic acid, found it well to dissolve the acid in neutral sodium sulfite and to treat the solution gradually with excess of 4 per cent sodium amalgam, while passing a continuous current of sulfur dioxide throught it.

Jacchia[56] found that the sulfonic groups could be removed from 2, 6-diamino-naphthalene-disulfonic acid by simply dissolving the acid in water, and adding solid sodium amalgam to the hot solution. After a few minutes, 2, 6-diaminonaphthalene separated as a greenish mass and was recrystallized from water. (Sulfurous acid could be detected in the reduced liquid.)

While other agents react with sulfoanthranilic acid, $C_6H_3 \cdot NH_2 \cdot COOH \cdot SO_3H$, in such a way that when they split out the sulfonic group, the carboxyl group is also partially removed, leading to the formation of aniline, sodium amalgam removes only the sulfonic group when it reacts in an aqueous solutions of the acid. For this purpose, 22 kgm. sulfoanthranilic acid[57] is dissolved in 500 liters water, neutralized with sodium carbonate, and 200 kgm. 5 per cent sodium amalgam added to the solution at room temperature. When gas is no longer evolved, the solution is acidified with acetic acid, and boiled down to cause the anthranilic acid to crystallize out.

Phenolic ethers were always saponified by the inconvenient treatment with hydrochloric acid in a sealed tube,[58] until Wohl,[59] in 1910, found that the phenol could be split off very easily by boiling with glacial acetic acid in the presence of sulfuric acid, most of the alcohol being converted into the corresponding acetate. For instance, he boiled 1 part phenyl phenetole $C_6H_5-CH_2-CH_2-O-C_6H_5$, for forty-eight hours, with 2 parts glacial acetic acid and 0.5 part 70 per cent sulfuric acid, and obtained a yield of 65 to 70 per cent of the theory of phenylethyl acetate, $C_6H_5-CH_2-CH_2-O_2-C_2H_3$, so valuable as a perfume.

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[55] Gattermann, L., and Schulze, H., *Ber.*, **30**, 51 (1897).

[56] Jacchia, A., *Ann.*, **323**, 131 (1902).

[57] Kalle & Co., German patent 129165 (1900); Fr. VI, 151.

[58] Phenolic ethers are smoothly hydrolysed by boiling with 48 per cent hydrobromic acid, the corresponding phenols and alkyl bromides being formed. —H. T. C.

[59] Wohl, A., and Berthold, E., *Ber.*, **43**, 2177 (1910).

DIRECT AND INDIRECT METHODS OF AVOIDING THE BREAKING OF SEALED TUBES; AUTOCLAVES

Since the explosion of sealed tubes cannot always be prevented, it is a common practice to take precautions to minimize the danger. On the other hand, there is an effort to eliminate these explosions by the use of metal tubes or suitably constructed apparatus. Long ago, Hittorf[60] imbedded the glass sealed tube in which he had put phosphorus and lead—the phosphorus was obtained as crystals after cooling—in burned magnesia, in an iron tube which could be closed by screw caps at both ends, and heated it in a direct flame. Bunsen recommended for his method of determining nitrogen, that about 0.3 gram of the substance, together with 5 grams cupric oxide, be placed in a dry glass bomb tube filled with hydrogen. This was then placed in a form filled with plaster of paris paste and after drying for 1 hour, it was heated to a dull red. Wöhler[61] heated glass tubes to 150° in a steam boiler, operating at about 5 atmospheres super-pressure. Since the tubes contained aqueous solutions, no explosion was possible, because under such conditions the tubes were subjected to practically the same internal and external pressures.

The newer methods fall into two classes. On the one hand, while continuing the use of glass sealed tubes, attempts are made to make their bursting almost impossible. On the other is the replacement of glass tubes by metal apparatus. Technical practice has solved the problem of working under high pressures without real danger of explosion, by using autoclaves. The writer believes the reason that this method has not been more generally adopted in laboratory practice is the following. Autoclaves must always be well screwed up if they are to remain tight, and years of experience have taught the technical workers how to do this. They have also learned to know when an autoclave damaged by usage must be replaced by a new one. A young chemist, like others who have had no technical experience, lacks this knowledge. The introduction of such autoclaves into scientific laboratories presupposed types designed particularly for them. In addition, substances are often used in laboratories which should be worked only in glass. If these are carelessly put into autoclaves they will corrode them, even if made of the best materials. Furthermore, in practice, autoclaves are only used after laboratory experiments have shown that they will withstand the pressures to be developed. But in scientific laboratories, when investigating unknown reactions, pressures often develop which cannot be withstood by even the best of autoclaves. An example of this will be given later.

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[60] Hittorf, J. W., *Pogg. Ann.*, **126**, 193 (1865); *J. B.*, **18**, 130 (1865).

[61] Wöhler, F., *Ann.*, **103**, 117 (1857).

The use of metal tubes with simple screw caps will now be discussed. The tubes of this type, having no safety device, in contrast to autoclaves, do not permit a gradual reduction of the pressure after the reaction is over. This is always worthy of consideration, and if they explode in the furnace they give rise to very dangerous situations. Willgerodt and Rampacher,[62] for instance, worked with such tubes. They used a thick walled wrought iron tube 50 cm. long, about 6 cm. in diameter, threaded at both ends. After closing one end with a cap, they charged the tube with 150 grams isobutyl alcohol, 190 grams of aniline and 275 grams zinc chloride. The other cap was screwed on, and the tube heated to 240° for six to eight hours. At this high temperature, the pressure was so great that the tube soon leaked. The only practicable seal was made by putting copper disks in the caps. At the end of the reaction, the tube had to be opened very carefully since there was considerable pressure within, even after complete cooling. The reaction product was a yellow, hard, homogeneous mass with a crystalline structure. (To recover the *p*-tertiary-butyl-aminobenzene from it, the solid was dissolved in concentrated hydrochloric acid, the solution cooled, and sodium hydroxide solution added until the zinc hydroxide which separated in large quantity, redissolved. The free base then collected as a dark brown oil on the surface of the liquid. It was taken up with ether and the latter distilled).

Engel[63] was the first to show that unsaturated acids combine directly with ammonia to form amino acids. High temperatures are usually necessary for this, and consequently Fischer and Schlotterbeck,[64] when converting sorbic acid into an amino acid, heated 10 grams of this acid with 150 cc. of aqueous ammonia saturated at 0°, for twenty hours, at 150°, since practically no reaction took place at 130°. As glass tubes usually break during this operation, they used strong iron tubes and emphasized the importance of good sealing. (The purification of the amino compound was very complicated; it had to be accomplished through the phospho-tungstate.)

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[62] Willgerodt, C., and Rampacher, Eberhard, *Ber.*, **34**, 3667 (1901).

[63] Engel, R., *C. r.*, **106**, 1677 (1888).

[64] Fischer, Emil, and Schlotterbeck, Fritz, *Ber.*, **37**, 2359 (1904).

The views of two authorities in this field are given. One of them has continued the use of glass tubes, the other has devised a metal apparatus for laboratories. Ullmann[65] has expressed himself as follows concerning sealed tubes. To have substances react under pressure and above their boiling points, experiments on a small scale are carried out in glass tubes. The bottoms of these are sealed off round, the tubes then charged, and finally drawn out to a point. They are placed in so called explosion, bomb, or tube furnaces, which allow uniform heating of the tubes and offer sufficient protection to the experimenter from scattered particles of glass if the tubes explode. It was pointed out above that such explosions are quite frequent and often involve the loss of valuable materials and the results of weeks of work. Wrought iron tubes, which may be closed, have been made, but these must be enameled, if acids are to be heated in them. It is significant that these tubes have found little favor, as they are very heavy and most inconvenient for lengthy operations

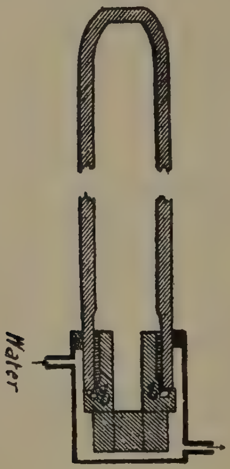

FIG. 94. ULLMANN-TUBE WITH COOLER FOR THE SEAL

such as extraction, emptying, etc. Furthermore, the enamel lining, and particularly the joints can hardly be guaranteed against attack by acids, etc. If the tubes are not perfectly tight, the experimental conditions change, or at least there is danger of losing valuable material and besides, the metal tubes lack the advantage of being transparent. If, then, such wrought iron tubes are only seldom suited to preparation work, there can be no thought of using them for quantitative purposes. The worker will always revert to the use of glass tubes which are clean, light, transparent, not readily attacked and may be hermetically sealed by fusing. But they have the disadvantage of being easily fractured by internal pressure.

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[65] Ullmann, Carl, *Ber.*, **27**, 379 (1894); German patent 68536, *Wagner's J. B.*, **39**, 1203 (1893).

To completely overcome this disadvantage or to considerably diminish the percentage of explosions, Ullmann started from the same principle used by Wöhler, cited above. If a glass tube is subjected to a somewhat greater, or equally as great a pressure on the outside as on the inside, the glass wall will not break, and likewise, if the external pressure is less than the internal pressure, the glass wall will have to resist only the difference of these pressures. Ullmann, therefore, puts the glass tube into a steel tube which is known to be able to resist enormous pressures. In the steel tube he puts a definite quantity of ether, benzene or other suitable liquid (at high temperatures water decomposes silicates, attacks the glass, and is, therefore, not suitable), then the glass tube containing the reaction material sealed as usual, closes the steel tube with the aid of vise and wrench and heats in the customary manner. The results of his experiments with different varieties of glass were as shown in table 5.

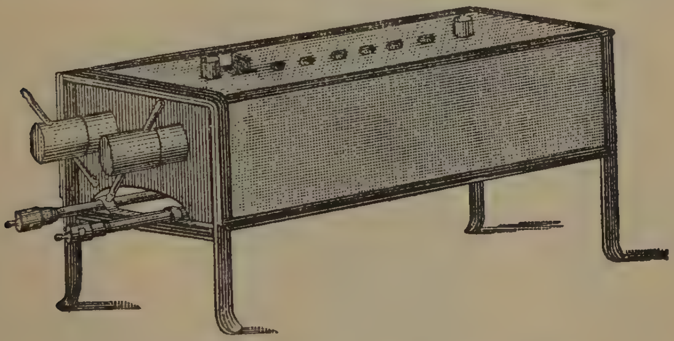

FIG. 95. BOMB FURNACE FOR ULLMANN-TUBES

A thin walled glass tube half filled with alcohol was kept at 275 to

280° for one hour, 60 to 70 cc. benzene and 30 to 40 cc. water were on the outside. The tube did not explode, its exterior was corroded by the water vapors and covered with a thick crumbling deposit, so that the walls were no longer as thick as an ordinary test tube. Muencke of Berlin recommends the following procedure: Steel tubes tested up to 600 atmospheres are charged with some (about 40 to 70 cc.) ether, dry benzene or similar materials (not water), the sealed tubes prepared as usual are inserted in the tubes of the furnace, the caps drawn on tightly using a vise and wrench and heated in the usual way. If the tubes are to be heated above 250 to 300°, the cooler is screwed on, and the joint cooled with water. If there is acid in the sealed tube, some lime may be placed in the steel tube for safety's sake. The renewal of the lead seal which is necessary to make the cap tight, is done by melting some lead in an iron kitchen spoon or porcelain crucible and pouring it into the channel of the inverted cap (fig. 96), so that a closed ring is formed which about half fills the channel. Then the cap (greased somewhat) is tightly screwed on the tube. The lead spreads over the surface *a*, and along *b* as far as the first threads of the tube. A seal of this kind is easily renewed. The tubes should be kept clean and free from rust, so it is best to rub them with some oil when not in use.

TABLE 5

Results of Ullmann's experiments

THIN WALLED CONDENSER TUBING ONE-THIRD FILLED WITH ETHER		THIN WALLED CONDENSER TUBING ABOUT ONE-HALF FILLED WITH 20 CC. HCl (SPECIFIC GRAVITY 1.19)		THICK WALLED POTASH GLASS. SULFUR DETERMINATIONS, 0.5 GRAM THIOCARBANILID 6 CC. HNO_3 (SPECIFIC GRAVITY 1.52)	
Exploded and pulverized at 190 to 192°	About 70 cc. ether on outside; remained whole at 222°	Exploded and pulverized at 187°	75 cc. ether and about 15 grams CaO on outside; remained whole at 220°	Exploded between 220 to 225°	70 to 80 cc. ether and 15 grams lime on outside; remained whole after 1½ hours at 265 to 270°

Pfungst[66] has endeavoured to replace glass sealed tubes, even in the laboratory, by autoclaves. He discusses the demands made on seals for tubes, which are to be used for experimental purposes, as follows: the joint must be absolutely tight so that the weight of the contents of the tube will not change during the heating; it must not be attacked by the material to be heated, even though this be acid or alkaline; it must withstand the internal pressure, even though large volumes of gases are liberated; it must not admit air when heating in a vacuum. Above all, the seal must offer the possibility of heating materials conveniently in a vacuum or in a medium consisting of any chosen gases or gas mixtures. At the end of the reaction it must permit the certain, quantitative collection of the gases formed in an easy and safe manner, even at greatly increased pressures. It must be possible to remove the seal completely and simply to permit very thorough cleaning of the inner walls of the tube.

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[66] Pfungst, A., German patent 53228 (1890); *Ber.*, **24**, R, 167 (1891).

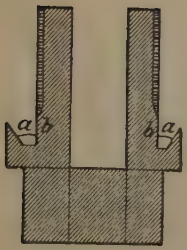

FIG. 96. TUBE SEALED WITH LEAD

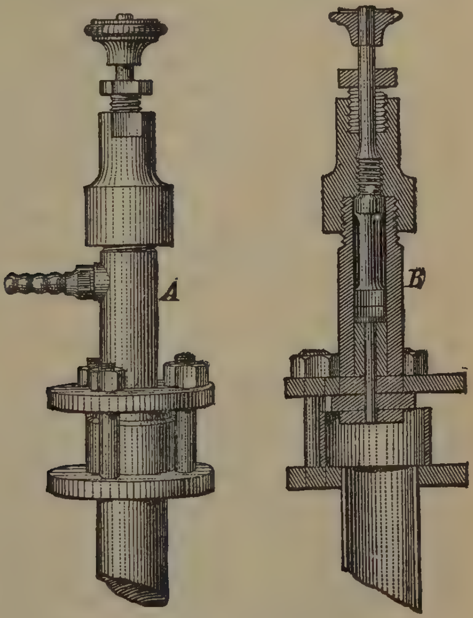

FIG. 97. LABORATORY AUTOCLAVE (PFUNGST)

Accordingly, the Pfungst apparatus[67] consists of 2 parts: The metal tube, and the cap whose exterior is shown in *A* and cross section in *B* (fig. 97). The entire length of the tubes is not reproduced. A later patent describes a somewhat modified cap. An extensive description of the apparatus, made of aluminium bronze or of iron coated on the inside with enamel or lead, is not essential here, since actual practice will soon give the necessary experience. It has the device requisite for evacuation of the tube before the start of the operation. The apparatus is heated in a copper oil bath. As a rule, the tubes are 350 mm. long and 40 mm. internal diameter. Each apparatus is tested cold up to 200 atmospheres pressure. Since the official test of steam boilers with cold pressure is double the steam pressure to which the boilers are to be subjected, these autoclaves are then designed for 100 atmospheres excess pressure, if heated.

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[67] Pfungst, A., German patent 56816 (1890); *Chem. Ztg.*, **15**, 963 (1891).

The Pfungst apparatus may also serve to subject sealed glass tubes to a very high external pressure, and in this way hinder their exploding, in somewhat the same way as do the Ullmann tubes. Thus, Noelting and Freyss[68] made Carius halogen determinations in the Pfungst apparatus, surrounding the tubes with 50 cc. of ether in order to obtain the desired pressure at 250°.

Walter[69] sought to solve the problem in a somewhat different manner than did Ullmann. Like him, he placed the glass tube in a steel tube, but developed the external pressure by carbon dioxide run in from a bomb. No one else seems to have used his apparatus. In his experiments[70] on reductions by phenylhydrazine, he heated 9 grams ethyl nitrate with 2 mols of this reducing agent in an autoclave which had been tested to 200 atmospheres, but even at 120° an explosion occurred which tore off the head of the autoclave.

In conclusion, mention is made of an apparatus constructed by Ipatiew,[71] in which it is possible to carry on experiments at 400 atmospheres pressure and at temperatures as high as 625°. The apparatus and experimenter alike have gone through innumerable experiments unharmed. Ipatiew has continued these experiments for many years and has even used many catalysts. Most of his work was done with an apparatus made of phosphor-bronze. But when, instead, he once accidentally used an iron tube and copper oxide as the catalyst, he obtained entirely different products from the same starting materials.[72] This led him to further extensive studies in this field.

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[68] Noelting, E., and Freyss, G., *Bull. de la Soc. ind. de Mulhouse*, **65**, 88 (1895); *J. Soc. Ch. Ind.*, **14**, 769 (1895).

[69] Walter, J., *J. pr. Ch.*, [2], **53**, 132 (1896).

[70] Walter, J., *J. pr. Ch.*, [2], **53**, 450 (1896).

[71] Ipatiew, W., *Ber.*, **37**, 2983 (1904); *Ber.*, **41**, 993 (1908).

[72] Ipatiew, W., *Ber.*, **43**, 3388 (1910).

CHAPTER IX

DECOLORIZING AND CLARIFYING LIQUIDS

About 1790 Lowitz noticed the decolorizing power of charcoal, and in 1828 Dumont introduced it into sugar manufacture. Even now charcoal is practically the only decolorizing agent used in laboratories, but a few other materials are of service. The other decolorizing and clarifying agents which will be discussed, precipitate, as does lead acetate, the materials to be removed (mostly coloring matter), or like fuller's earth and kieselguhr, they act mechanically through a kind of surface attraction. The action of charcoal also may finally be due to surface attraction. It may happen that this property of charcoal and other adsorbent materials may be used directly for the preparation of the material they adsorb, as shown below.

DECOLORIZING BY ANIMAL CHARCOAL

Pure blood charcoal is the best for laboratory purposes. Skraup[1] cautions particularly against preparations containing iron, and the writer adds a warning against those containing copper. According to Knecht,[2] the treatment of animal charcoals with hydrochloric acid, followed by hydrofluoric, may reduce the ash content of blood charcoal to 0.6 per cent and of bone charcoal to 0.4 per cent. Since animal charcoal has a strikingly higher decolorizing power than wood charcoal, numerous samples of animal charcoal were investigated, and 5 to 7 per cent of combined nitrogen was found in each of them, while only a trace of this element was found in a sample of wood charcoal. Animal charcoal also contains about 0.5 per cent sulfur. These constituents cannot be accidental impurities and may be responsible for the different action of animal and wood charcoal toward coloring matter. The nitrogen has never been entirely removed from animal charcoal, but 32 hours ignition reduced it from

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[1] Skraup, H., *Monatsh.*, **1**, 185 (1880).

[2] Knecht, Edmund, *Ch. Zt. Repertorium*, **31**, 435 (1907).

5.76 to 3.61 per cent. The two samples were "dyed" on the water bath for 1 hour with a large excess of crystal ponceau in the presence of acid and the quantity of dye not adsorbed then determined with titanous chloride. The quantity of dye taken up by the two samples was directly proportional to their nitrogen content. Blood and bone charcoal gave the same results.

van Os[3] states that decolorizing charcoals are best assayed by the method of Wiechowski with methylene blue and of Joachimoglu with iodine. There is a question whether these methods suffice for all practical purposes, and whether decolorizing experiments with methylene blue and iodine solution really indicate the variety of charcoal best suited to a particular case. Furthermore, he found that a cellulose charcoal gave very high values by these methods, but decidedly lower ones when tested with solutions of caramel and of quinine hydrochloride. He concludes that the assays must always be considered from the standpoint of the purpose and of the method of using the charcoal.

Many ether solutions, as obtained, say, in extractions, are decolorized, even in the cold, by good animal charcoals if they are allowed to stand in contact for 24 hours, with occasional shaking. It is well to combine this method of decolorizing with simultaneous dehydration of the liquid, by adding to it anhydrous sodium sulfate, calcium chloride or similar materials in addition to the animal charcoal.

Decolorizing in the cold is exceptional. In general, the liquid to be decolorized must be boiled with the animal charcoal and sometimes this boiling must be continued for hours.[4] Experience is continually showing that finely powdered charcoals and especially blood charcoal, are carried through filters in small quantities.[5] Therefore, materials should never be used for ultimate analysis which have been crystallized from solutions decolorized by charcoal, but they should first be redissolved, filtered, and then recrystallized, so that the rest of the charcoal will remain on the filter. If the charcoal which was used for the first decolorization and remains on the filter, is boiled up with alcohol, for example, and the latter then used for this second recrystallization, there will be recovered, at the same time, most of the material which usually adheres to the charcoal originally used.

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[3] van Os, D., *Pharm. Weekbl.*, **57**, 693 (1920).

[4] Bamberger, E., and Philip, M., *Ann.*, **240**, 169 (1887).

[5] In this connection may be mentioned Liebig's experience with the combustion of allantoin which retained traces of charcoal which had been used in decolorizing it and gave wrong results. See in Liebig's reminiscences, *Ber.*, **23**, R, 819 (1890).

ACTIVATED CHARCOAL[6]

A new decolorizing charcoal was obtained in the following way:[7] Because of the strong dehydrating action of zinc chloride on carbonaceous materials, like cellulose, sawdust, etc., progressive heating of a mixture of zinc chloride with the carbonaceous material until the zinc chloride distils, causes complete carbonization of the material, and separates the carbon in a form possessing very high decolorizing properties and surprising adsorptive powers. Activated charcoal is now widely used in technical practice. Its ability to adsorb organic gases and gasified organic substances from their mixtures with air or other gases, is so great that it has been the subject of a patent. The vapors of alcohol, ether, benzene, etc., are taken out of the air quantitatively by the charcoal, and then may be expelled from it by superheated steam and recovered. At the same time, the activated charcoal is rejuvenated with its original power. Other methods of using charcoal for the recovery of materials will be given later.

AFFINITY OF CHARCOAL FOR MATERIALS OF ALL KINDS

Bitter principles, etc.

Charcoal retains materials of many kinds as well as dyes and vapors so tenaciously that methods of preparing certain substances may be based upon this property. For example, Liebermann[8] found that potassium urate was particularly retained. The same is true of salts of aromatic acids, so that serious losses may result from this. It even decomposes the salts of fatty acids so that the free acids may be detected in the filtrates. It exerts the same action on the salts of alkaloids, such as morphine acetate, caffein citrate. These dissociations only occur in aqueous and not in absolute alcoholic solutions.

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[6] The intensive study that has been given to the preparation of active charcoal for gas masks has produced many varieties some of which are many times more active than any previously known.—E. E. R.

[7] Oesterreichischer Verein für Chem. Produktion, German patent 290654 (1914); *Chem. Zent.*, 87_{I}, 594 (1914); see also Farben Fabrik vorm. Bayer, German patent 310092 (1916); *Chem. Zent.*, 92_{II}, 216 (1921); *Austrian patentanmeldung* Nr. A 4831; see also, Harned, H., *J. A. C. S.*, **42**, 372 (1920); Lamb, A., and Coolidge, A., *J. A. C. S.*, **42**, 1146 (1920).

[8] Liebermann, L., *Sitzungsber. Wiener Akad.*, [2], **75**, 331 (1877).

Hopff was the first to point out that wood charcoal, and also particularly animal charcoal, can withdraw the bitter principle from the extracts of many plant materials. This may occur in the cold and is certain to happen during boiling. According to Kromayer,[9] bone black is best suited for removing the bitter principles from such extracts. It works best when fine grained, because only then may it be washed out easily and rapidly, whereas powdered charcoal has many disadvantages from this standpoint. Any ammoniacal products adhering to it are removed by washing it with water for a long time, and then freshly igniting it. Thoms[10] obtained 0.29 gram bitter material from 300 grams calamus root and Guether[11] boiled the extract of this root with animal charcoal until the taste showed that the charcoal had taken all of the bitter principle out of the solution. He then dried the charcoal and extracted the principle from it by boiling with 99 per cent alcohol.

CHLORINE

Chlorine bleach is a well known decolorizing method. However, in laboratory practice, chlorine has seldom been used with solutions of various kinds because it was assumed that there was danger that the product to be decolorized would then contain chlorine. Technically, however, chlorine is said to be very useful for bleaching substances which are present in the solution along with dye stuffs from the time of their preparation. It is said that small quantities of chlorine are added to the liquid to destroy the by-products[12] before certain dyes are salted out from their slightly impure solutions by sodium chloride. The absorption spectra are particularly useful in determining to what degree red coloring materials, for example, may be further purified by careful addition of chlorine water. In this way, it should be possible to avoid subsequent addition of a white powder to the red dye powder, as is now occasionally necessary.

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[9] Kromayer, A., *Die Bitterstoffe*, Erlangen 1861, p. 18.

[10] Thoms, H., *Arch. Pharm.*, **224**, 465 (1886).

[11] Geuther, A., *Ann.*, **240**, 94 (1887).

[12] Henry, C., French patent 376084 (1907); *Ch. Zt. Repertorium*, **31**, 495 (1907).

SULFUROUS ACID; SODIUM HYDROSULFITE; SODIUM HYPOPHOSPHITE

Besides animal charcoal, sulfurous acid is used for decolorizing. For example, Knorr[13] decolorized, in this way, methyl alcoholic solutions of antipyrine. Although it plays a minor rôle in the laboratory, this is not the case in technical practice. For about thirty years it has completely eliminated bone charcoal from the manufacture of crude sugar, since it has replaced it for decolorizing the juices, and consequently has done away with the troublesome and disagreeable rejuvenation of the bone black.

The salts of hydrosulfurous acid, which come into the trade under various fantastic names, may also be used as decolorizers. They are used less in laboratories than they deserve to be. A technical application is given here which may serve as an example. The bleaching of soap by sodium hydrosulfite $Na_2S_2O_4$ ("blankite") seems to be due to the reduction of the iron and occasional manganese salts present in practically all soaps. The use of the "blankite"[14] in this industry is very simple. Dry hydrosulfite amounting to 0.2 to 0.3 per cent of the weight of the fat, is added to the kettle and distributed as rapidly and uniformly as possible. A solution of hydrosulfite in water to which soda lye has been added, may also be used. The poorer the fat used for the preparation of the soap, the more is its color lightened.

Hypophosphite also does not appear to have been used in the laboratory. The process is based, according to Dufour,[15] upon the observation that mixtures of hypophosphites and sulfites in acid solution, show great decolorizing properties so that they may be used advantageously for decolorizing tannin extracts, for example. (The addition of formaldehyde considerably increases these properties.) For instance, to quebracho extract (1000 kgm. 24°Bé.) liquefied by warming, is added 3 kgm. sodium hypophosphite, 15 kgm. bisulfite dissolved in a little water, and 5 kgm. of 40° Bé. sulfuric acid. This is all heated for several hours at 60 to 80°, and a powerful decolorizing is observed. Chestnut extract is treated in a similar manner: 1000 kgm. 25° Bé. are decolorized with 5 kgm. sodium hypophosphite, 20 kgm. bisulfite, 7 kgm. sulfuric acid (40°Bé.) and 5 kgm. formaldehyde solution (40 per cent).

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[13] Knorr, L., *Ber.*, **17**, 549 (1884).

[14] *Ch. Zt. Repertorium,* **31**, 434 (1907).

[15] Dufour, L., French patent 367917 (1906); *Ch. Zt. Repertorium,* **31**, 295 (1907).

DECOLORIZING BY PRECIPITATING AGENTS

Neutral or basic lead acetate is most commonly used for precipitating dyes. According to Fischer,[16] pure double basic lead acetate is much more efficient than ordinary basic acetate, because it precipitates many materials not precipitated by the latter. Löwe[17] states that this double basic lead acetate $Pb(C_2H_3O_2)_2 + 2\ PbO$, is obtained if 500 cc. of a solution of lead acetate saturated at intermediate temperatures is mixed cold with 100 cc. ammonia (d. 0.96) in a tightly stoppered flask. After several days, it crystallizes out abundantly. The crystals are washed on the filter with a little distilled water. They dissolve completely even in cold water.

The liquid to be decolorized may be a water or alcoholic solution. It may react neutral or alkaline, but the procedure is always to add neutral or basic lead acetate solution until the filtrate is clear, and, if possible, water clear. The filtrate is then freed of lead by hydrogen sulfide or by careful addition of sulfuric acid. Sometimes the last of the coloring matter is only carried down with the lead sulfide precipitate.[18] If basic lead acetate is to be used in alcoholic solution, 4 or 5 times its weight of alcoholic ammonia is first added. This produces a clear alcoholic lead solution.

It is well to note that basic lead acetate precipitates, besides dyes, many other indifferent compounds, such as all glucosides. According to Schmiedeberg,[19] as a rule, rubber and plant mucilage are precipitated by even neutral lead acetate, and certainly by a solution of sugar of lead; while the soluble carbohydrates, in aqueous solution, precipitate with neither, but are thrown down as lead compounds only after the addition of ammonia. This fact is of particular interest in working with plant extracts, as, for instance, when recovering alkaloids from them.

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[16] Fischer, Emil, *Ber.*, **27**, 3195 (1894).

[17] Löwe, J., *J. pr. Ch.*, [1], **98**, 397 (1866).

[18] Fischer, Emil, and Piloty, Oscar, *Ber.*, **24**, 4216 (1891).

[19] Schmiedeberg, O., *Z. physiol. Ch.*, **3**, 114 (1879).

This subject is also of interest with reference to urine analysis.[20] The urine of the sick often contains sugar and, as Brücke[21] has pointed out, it is very important to know that although a solution of lead acetate alone produces no precipitate with pure sugar solutions, nevertheless, a slight precipitate containing part of the sugar is produced by it from synthetic and pathological sugar urines. Sugar in urines is frequently determined quantitatively by means of the dextro rotation which it exhibits in a polarizing apparatus. However, the urines are practically always so highly colored that direct reading of the polarimeter is impossible and, therefore, they must be decolorized. (It should not be forgotten that any albumen present must first be removed because it is laevo-rotatory and consequently compensates part of the rotation due to the sugar.) In a quantitative analysis, when decolorizing urines containing sugar, or sugar juices, the volume of the lead acetate solution must be known so that the dilution produced by it may be taken into consideration. The writer prefers to avoid this inconvenience by decolorizing all urines with a trace of the best blood charcoal. This is easily done and requires no measuring vessels.

As mentioned above, many compounds do not precipitate on the addition of lead acetate alone, but only after the subsequent addition of ammonia. Many other bases may be used in place of the ammonia. Thus Fischer[22] precipitated ribose as a lead compound from its solution, by adding an excess of basic lead salt, and then baryta water sufficient to precipitate the lead. He obtained ribose almost free from ash by treating the washed precipitate with sulfuric acid and then evaporating the filtrate.

It is apparent that the decolorizing of solutions with lead acetate may be combined with the preparation of materials much more readily than can the treatment with animal charcoal. Many coloring matters in particular, can only be obtained from their solutions, by recovering them from the precipitated lead compounds.

Although laboratories use practically nothing but lead acetate, a patent[23] particularly recommends stannous chloride, and it may be that this material would be useful in many scientific studies. The dark, tarry crude solutions of hydroxyacids such as salicylic, anisic, cresotinic, as well as of phenol and its homologues which cannot be successfully treated with materials like zinc chloride (!) or by reducing agents such as ferrous chloride or sulfurous acid, may be well purified by stannous chloride according to the claims of this patent. Thus the crude solutions of salicylic acid produced by the famous, but now superseded Kolbe process, are treated, while being slightly heated and stirred, with stannous chloride solution until the liquid separating from the precipitate is water clear. The salicylic acid precipitated from this filtrate by hydrochloric acid may be termed pure after it has been washed free of chloride. (As is known, salicylic[24] acid is now produced far more conveniently than by the Kolbe method, so that this purification is no longer of importance in the preparation of this compound.) F. Thiele[25] states that in South America, stannous chloride solution is used to obtain crude sugar of a brighter color from the cane, 2.5 to 5 kgm. of stannous chloride being added to about 15,000 kgm. of the sugar, during the vacuum boiling. In the centrifuge, after one wash with water, the crystals are again washed with a very dilute solution of stannous chloride. About twenty years earlier, Hlasiwetz and Habermann[26] found that very dark solutions were obtained if egg albumen was converted into a mixture of amino acids, etc., by boiling with hydrochloric acid. If, however, stannous chloride is previously added to the mixture, it remains much brighter and the preparation in a pure state of the products formed is much simpler. They, at that time, did not regard it as a decolorizing agent, but as a means of hindering the formation of undesirable coloring matters. It may be useful in many other cleavages with hydrochloric acid.

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[20] See also the comments on urine analysis, p. 9.

[21] Brücke, E., *Sitzungsberichte d. math. nat. Klasse der Akad. d. Wissenschaften zu Wien*, **39**, 10 (1860); see also Borntraeger, A., *Archiv. Pharm.*, **216**, 447 (1880); *Ch. Zt.*, **7**, 1655 (1883).

[22] Fischer, Emil, and Piloty, Oscar, *Ber.*, **24**, 4220 (1891).

THE CLARIFICATION OF LIQUIDS

In general, liquids may be clarified by filtration. If very fine precipitates which pass through the filter are distributed through them, these are enveloped in coarser precipitates, if possible, so that they will be retained. For example, some lead acetate or barium chloride solution is added to the liquid and then a little sodium carbonate solution,[27] and the lead or barium carbonate formed carries the fine precipitate down with it. However, this often introduces undesirable salts into the solution. But a proper choice of the added materials may obviate this, by causing them to mutually precipitate each other. Thus Schenk[28] has found the action of nascent alumina in combination with nascent barium sulfate, to be particularly suited for clarifying liquids containing tannin. His procedure was as follows: the hot tannin solutions to be purified were treated with a solution of aluminium sulfate, each according to the extract content of the solution. After thorough mixing, an equivalent quantity of barium hydroxide was added, and the system cooled to about 20°, while stirring continuously. In one instance, 1000 liters of quebracho extract 4°Bé., required 2 kgm. aluminium sulfate and 0.944 kgm. barium hydroxide. He claims that the turbid liquids produced settled very rapidly, and could be filtered perfectly clear. The double decomposition produced barium sulfate and aluminium hydroxide both of which remained on the filter. Alumina alone, in the form of colloidal alumina,[29] had previousy been recommended for clarifying.

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[23] Hofmann, P. W., German patent 65131 (1892); Fr. III, 826; German patent 67696 (1892); Fr. III, 827.

[24] Marasse, S., German patent 78708 (1894), Fr. IV, 152.

[25] Thiele, F. C., *Ch. Zt.*, **25**, 563 (1901).

[26] Hlasiwetz, H., and Habermann, J., *Ann.*, **169**, 150 (1873).

KIESELGUHR; FULLER'S EARTH; LOAM

Animal charcoal, in contrast to precipitating agents, decolorizes solutions without chemical action. Kieselguhr likewise, without chemical action, will produce clear filtrates from turbid solutions, which of themselves will not filter clearly. At the beginning of the sixties, Krall[30] patented the purification of sugar juices by filtering them through kieselguhr. This method of clarification is now obsolete.

Among the liquids which cannot be filtered clear by methods employed in chemical (not bacteriological) laboratories, are the putrescible ones, since the putrefactive bacteria are smaller than the pores of the filter paper and pass through it, making the filtrate turbid. If such liquids are thoroughly shaken with kieselguhr as recommended by Jolles,[31] a clear filtrate will be obtained. This procedure is often of great value, especially for biochemical work of all kinds. This method may also be used with urines, which are frequently made turbid by bacteria. They then may be filtered clear through ordinary filter paper. Traces of albumen may be detected in them after this treatment, by the turbidity produced by boiling, and not dissipated on the addition of a drop of acetic acid, or other usual tests may then be applied for this purpose. Formerly, no method was known for detecting the albumen in such urines. The writer clarifies urines by filtering them through the crude kieselguhr such as is used for packing in shipping cases containing bottles of chemicals. The surface affinity of kieselguhr will be found to serve not only to retain bacteria but to bring about intimate contact of materials that are to react with each other and thus produce quantitative yields not possible in its absence.

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[27] Salkowski, E., *Z. physiol. Ch.*, **9**, 493 (1885).

[28] Schenk, H., German patent 71309 (1892); *Chem. Zeit.*, **17**, 1793 (1893).

[29] Löwig, E. and K., German patent 6713 (1878); *Chem. Ind.*, **2**, 285, (1880).

[30] Kral, H., *Ch. Zt*, **17**, 1487 (1893); von Lippmann, E., *Ch. Zt.*, **17**, 1551 (1893).

According to Parsons,[32] fuller's earth is a clay consisting of an aluminium silicate with a high content of combined water. It has high adsorptive properties for coloring matters and consequently bleaches fats and oils and also petroleum, etc. To attain the full decolorizing power of the fuller's earth it is necessary to previously dehydrate the oil to be bleached. This is a point of particular interest in comparative experiments. There are cases in which silicates are better decolorizers than the charcoals. In the eighties, the writer had to furnish many millions of kilos of so called "decolorizing powder," which remains after the extraction of the masses obtained by heating animal products with potash in the old ferrocyanide industry, as this was used for decolorizing Galician earth wax. This is now obsolete and better results are obtained, according to Lach,[33] by using Frankonite or Tonsil, two aluminum silicates, because they bleach the earth wax incomparably better than the "decolorizing powder." In the paraffin industry, the powder has been replaced by magnesia hydrosilicates which have practically no bleaching action on earth wax.

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[31] Jolles, A., *Z. anal. Ch.*, **29**, 407 (1890).

[32] Parsons, C., *J. A. C. S.*, **29**, 598 (1907).

[33] Lach, B., *Ch. Zt.*, **37**, 573 (1913).

As an instance of the use of fuller's earth, crude beeswax[34] is heated to about 130°, with constant stirring, and about 10 per cent of the earth added in small portions. The temperature is gradually raised to 150 to 170°, the fuller's earth takes up the coloring materials and finally becomes black, while the beeswax foam gradually becomes white. After sufficient bleaching, which requires about 30 minutes, the heating is discontinued and the wax, while still hot, is separated from the residue by filtering or centrifuging. The residue contains 40 to 50 per cent of wax which may be extracted from it with carbon disulfide or carbon tetrachloride.

Finally, besides kieselguhr, loam is also used technically as a clarifier, especially in the preparation of milk sugar. The solid portion is separated from curdled milk and the whey is concentrated first on the water bath and then over the free flame, until the earthy phosphates precipitate. The residue is again diluted with water and there results a solution that is turbid because of albumen particles and which cannot be filtered clear without further treatment. In this large industry, in certain places, this clear filtration is accomplished by thoroughly stirring the solution with some loam before filtering. The milk sugar is then crystallized from the filtrate after it has again been carefully evaporated.

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[34] Miller-Jacobs, A., United States patent 883661, *Chem. Abstr.*, **2**, 2457 (1908).

CHAPTER X

EXTRACTION BY MEANS OF LIQUIDS BOILING UNDER A REFLUX

The extraction of materials by cold solvents or by solvents boiling in open vessels is treated under the heading "Solvents and Diluents."

EXTRACTION OF SOLIDS

A great number of devices have been constructed for the extraction of solids with liquids of high or low boiling points. When working with extraction apparatus having double jackets, the heating of solvents boiling below 100° is best done by the vapor of the solvent itself. The temperature developed does not exceed the boiling point of the solvent, and this insures against the disturbing generation of vapor in the extraction chamber which may occur if steam is led into the double jacket. If rather impervious masses are to be extracted, they are melted together with enough extracted sawdust[1] or other suitable material, so that they become sufficiently penetrable after being cooled and broken up.

It is often difficult to make tight connections in extraction apparatus by means of corks, which come in contact with boiling ether, benzene, etc. Such apparatus is now usually made of parts ground to fit each other. Some years ago, Neumann[2] proposed chrome-gelatine as a reliable sealing agent since it is insoluble in water and the solvents named above, after it has been exposed to the light. The chrome-gelatine is prepared by dissolving 4 parts of gelatine in 52 parts of boiling water, filtering, and then adding 1 part ammonium dichromate. The parts of the apparatus to be sealed are coated with this solution by means of a brush and are then exposed to the light for two days.

The following example shows what errors may arise from cork connections. Barrier[3] found, in a series of gum analyses, using acetone in a Soxhlet apparatus with cork stoppers, that in spite of 90 hours' extraction, it was almost impossible to attain constant weight. An investigation of the cork stoppers finally gave the reason. A white resinous mass had separated from the cracks of the cork. From 4.18 grams of cork cut into small pieces 0.2080 gram of this material was obtained by extraction with acetone, whereas, the total weight of extract attained in gum analyses seldom exceeds 0.0600 gram.

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[1] Lach, Bela, *Ch. Zt.*, **37**, 573 (1913).

[2] Neumann, G., *Ber.*, **18**, 3064 (1885).

[3] Barrier, E., *J. Am. C. S.*, **29**, 1242 (1907).

Stanek[4] discusses cork seals as follows: Everyone who must frequently determine fats or other materials by extraction with ether or alcohol, recognizes the undesirable features of cork stoppers. On one hand, there are the losses of solvents caused by the great porosity and defects of the cork, and on the other, the fact that many materials present in the cork dissolve in ether, and particularly in alcohol. These substances later contaminate the extract, and the cork shrinks and crumbles. (This latter disadvantage is especially marked in the case of the cork substitute "suberite." A stopper of this material, exposed for several days to alcohol vapors, shrank, when dried, to one-third of its volume.) He has obviated this evil by preparing cork stoppers so that they close the extraction apparatus as tightly as possible, and then covering them with thin tin or lead foil. Gum arabic, gelatine, water glass and other materials may be used as adhesives, and would not be affected by the extraction medium. The curved surfaces are covered with 4 to 5 layers of tin foil, the under surface with a double layer, all glued together, and allowed to dry. Any necessary openings, whose walls should be as smooth as possible, are then cut with a sharp cork borer placed on the tin foil surface. Cork stoppers prepared in this way are perfectly impermeable to vapors, make tight joints, and their volume does not change even after several months' use. Rubber stoppers are little suited for this purpose; many solvents partially dissolve them and practically all swell them badly.

All of the liquids mentioned under the headings "Extraction" and "Crystallization" may be used for extraction, provided they boil without decomposition, if their boiling points are not too high. According to Hefter,[5] an extraction medium should volatilize easily and completely and leave no odor. Furthermore, it should be a uniform material so it will suffer no fractionation when distilled, since this may soon cause irregularities in the outflow of the extraction liquids.

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[4] Stanek, Vl., *Ch. Zt.*, **30**, 347 (1906); also Kolbe, G., *Ch. Zt.*, **32**, 421 (1908).

[5] Hefter, *Technologie der Fette und Öle*, I, p. 348.

It is also often desirable that extraction media be non-inflammable, and, if possible, not act on metals. Benzene and carbon bisulfide, so much used in factory practice, cause a high fire risk, while the non-inflammable carbon tetrachloride, which is also widely employed, attacks iron, copper and zinc in the presence of moisture, so that it may be used only in lead lined apparatus. Accordingly, the following derivatives of acetylene tetrachloride[6] have been placed on the market:

Dichlorethylene (sym)	$C_2H_2Cl_2$	B.P. 55°
Trichlorethylene	C_2HCl_3	B.P. 88°
Perchlorethylene	C_2Cl_4	B.P. 121°
Tetrachlorethane (sym.)	$C_2H_2Cl_4$	B.P. 147°
Pentachlorethane	C_2HCl_5	B.P. 159°

These liquids constitute a series of indifferent and very stable solvents and extraction media whose boiling points range from 55° to 159°, so they can meet a great variety of demands as to extraction temperature and volatility. All of them are non-inflammable and they carry no danger of explosion. Even in the presence of water, they are indifferent toward metals, even toward wrought iron, and do not act on fats and oils.

The Soxhlet apparatus is most commonly used for extractions. In it, the liquid distilled up remains for some time in contact with the material to be extracted, and is finally returned to the boiling flask through an overflow which acts as a syphon. The material to be extracted is supported by cotton wool, or it is put into a paper shell made of fat-free filter paper, obtainable in sizes suitable for the purpose in hand (fig. 99). A Walther bulb or similar condenser may be used in place of the Liebig condenser, to reduce the height of the apparatus (figs. 98, 100).

The writer had a Soxhlet apparatus made of copper for the extraction of larger quantities of solids. It has a capacity of 4 liters and is tinned inside. Its lower opening is connected with a large round bottom flask by a cork, as in the glass apparatus. It is closed by a cover provided with thumb screws, in the center of which is a removable piece of tubing which leads through a cork to an ordinary condenser which acts as a reflux. On the bottom of the metal apparatus is placed a gauze, over this a layer of cotton wool and then another gauze to prevent the material to be extracted from clogging the outlet. The flask in which the extraction liquid is contained during the long heating is protected from breaking by being placed in a bath. On one occasion, when the writer was extracting several kilos of tea with water, he used a calcium chloride bath boiling at

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[6] Consortium für elektrochemishe Industrie, Nürnberg, *Ch. Zt.*, **31**, 1095 (1907).

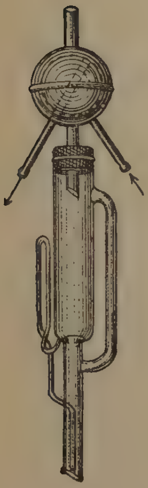

FIG. 98. EXTRACTION-APPARATUS WITH BALL CONDENSER (SOXHLET)

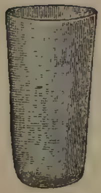

FIG. 99. PAPER THIMBLE FOR EXTRACTION APPARATUS

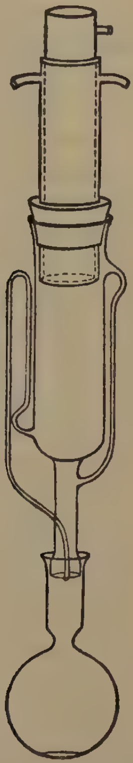

FIG. 100. EXTRACTION-APPARATUS WITH WALTHER CONDENSER (SOXHLET)

about 170° and the extraction proceeded for days without any trouble.

It is a great disadvantage to anyone who works with a Soxhlet apparatus, and wishes to save time and gas, and accordingly does not wish to prolong the extraction process longer than necessary, that the removal of samples of the filtrate is so inconvenient and cannot be done without taking the apparatus apart. Ordinarily, the extraction is prolonged far longer than is necessary to insure removal of all soluble materials. Yet Hagen[7] has devised a simple means of obviating this difficulty. As shown in figure 101, it is only necessary to bend the tube rising from the bulb *F* into a circular loop *S*, and to provide this with a cock *H* opening at right angles and so placed that the upper end of the opening is somewhat below the overflow on the inside of the loop. The liquid constantly running from the extraction cylinder will gradually fill the loop, and run back into the flask if the cock is set as shown. If, however, the cock is turned at 180°, the liquid is emptied to the outside through the small spigot. It is thus possible to withdraw samples of the filtrate by simply turning the cock, and without taking the apparatus apart and interrupting the analysis. The loop affords another advantage. It makes the syphon tubes of the ordinary apparatus unnecessary, and these are not only easily broken, but they do not completely empty the extraction cylinder, because when the syphon acts, part of the liquid always flows from the small tube back into the cylinder. Likewise, the filter whose emptying cannot keep pace with that of the cylinder, empties some more liquid into the cylinder after the syphon action is over. If this again is filled with condensate from the condenser, the liquid containing the soluble material again comes in contact with the substance; obviously this unduly retards the extraction. In the new design, the condensate drops upon the material to be extracted, takes up soluble material and runs off unhindered and completely. In this way, the substance is constantly irrigated with fresh, pure solvent, and naturally the extraction of the soluble materials is completed in much less time. If it is important that the liquid dropping from the condenser should arrive as close as possible to the center of the filter, a funnel is placed in the upper wide part of the extraction cylinder by means of a cross piece

[7] Hagen, Oskar, *Ch. Zt.*, **45**, 19 (1921).

and knob *R*. It is not absolutely necessary that it be ground to fit the conical surface *G*, since the hydraulic seal in the loop *S* forces the vapors arising from the flask *F* to pass, for the greater part, through the side tube. The substances are placed in the vessel *G* proposed by Frühling,[8] which has a ground cover and can be conveniently set on the balance as well as in the drying oven, and so the sample can be accurately weighed before and after the extraction. It is convenient to have a small cap ground to fit the lower exit to hinder the absorption of moisture by the filter and extraction residue after they have been dried.[9]

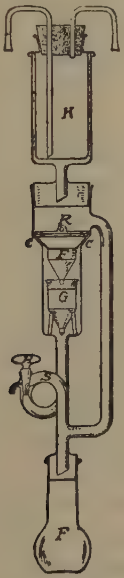

FIG. 101. SOXHLET'S EXTRACTION-APPARATUS WITH SAMPLER (HAGEN)

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[8] Frühling, R., *Z. angew. Ch.*, **2**, 242 (1889).

[9] The extraction of soluble matter from solids may be efficaciously carried out, on quantities varying from a few grams to half a kilo, by placing the powdered solid on a folded filter paper on a sufficiently large funnel which is stoppered to a flask containing the boiling solvent. Condensation is effected by means of a round bottom flask partly filled ~~with cold, running water, which~~ completely closes the wide end of the funnel. This apparatus is illustrated in Organic Syntheses, **2**, 49 (1922). In a modification due to Bloor and Sperry (*J. Biol. Chem.*, **68**, 36, 359 (1926)) the paper is replaced by a cloth bag and the funnel by a percolator.—H. T. C.

The problem of extracting fat from materials of various kinds, requires special discussion. Thus, if fat is to be extracted from flesh, the dried flesh must be extracted with dry ether (see the later discussion of the use of acetone) because wet ether also dissolves other materials that will be finally weighed along with the fat. Wet ether gives a determination of "crude" instead of pure fat.[10] Accordingly, in more exact determinations, care must be taken that materials are not present during extractions with dry ether which, because of insufficient drying, may give up water to it. A case of this kind arises in the separation of fats from unsaponifiable, ether-soluble materials, or in the recovery of fat-free cholesterol and similar materials from fats. In such instances, the procedure of Juckenack and Hilger[11] is followed, the mixture being completely saponified by refluxing with alcoholic sodium hydroxide. Sand is added to the saponified mass which is then evaporated to dryness in porcelain dishes on the water bath. The sand is prepared for use by heating it strongly, treating it with hydrochloric and nitric acids, and then washing with water. In these very accurate experiments it must be dried and then extracted with ether. The soap mixtures obtained as above are then completely dried in vacuo over potassium hydroxide and then extracted for twenty hours in an extraction apparatus with ether dried over metallic sodium. The resulting ether solution containing traces of suspended soaps is placed in the ice box for twenty-four hours and filtered through a filter which has been well washed with anhydrous ether. The residue from this solution then contains the unsaponifiable constituents of the original material. In this case, saponification with potash solution is not suitable because the soda soaps dry much more easily. See the discussion of emulsions in the heading "Extraction", for treatment of any emulsions formed.

According to Rammstedt,[12] fat is determined in oil seeds, oil cake, etc., by grinding the material with quartz sand and drying it for thirty minutes at 100° in a vacuum drying oven before extracting it. After two and one-half hours extraction, the material is ground again and re-extracted for the same period. In this case, carbon tetrachloride may give figures 1 per cent above those found with ether. Since too much fat is obtained by ether extraction—because the ordinary ether extract is well known not to be pure fat, but a mixture of fat with varying quantities of other materials also soluble in ether, such as lecithin, chlorophyll and organic acids—it is certain that the value obtained by a simple exhaustive extraction with carbon tetrachloride is too high.

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[10] Voit, E., and Krummacher, O., *Z. Biol.*, **35**, 566 (1897).

[11] Juckenack, J., and Hilger, A., *Arch. Pharm.*, **236**, 369 (1898).

[12] Rammstedt ,Otto, *Ch. Zt.*, **33**, 93 (1909).

Experience has shown that the absolute quantitative extraction of thoroughly dried, pulverized meat, casein, etc., can hardly be accomplished. Thus Argutinski[13] has often extracted dry flesh, the preparation of which is described under the heading "Drying of Solids," for weeks without complete success. It is true that the greater portion of the fat is obtained the first day, the amount extracted the second being hardly $\frac{1}{20}$ to $\frac{1}{30}$ of that yielded the first day, but evaporation of the ether on the third and fourth days always left some fat in the residue. This was not reduced to a few milligrams until the fifth and sixth days. It was necessary to stop then because he was never able to obtain ether entirely free from residue, even though the extraction was continued longer. The writer had the same experience with thoroughly dried, powdered casein.

It is much better to use acetone for all fat extractions in place of the ether which is chiefly used in the laboratory for this purpose. The patentee Viss[14] has given the reason for this. He points out that materials are freed of fat and of water by first removing the water by means of alcohol and then the fat with ether, and therefore, it is much better to use acetone for this, because only one solvent, instead of two, is necessary. Furthermore, the use of alcohol has the disadvantage that the recovery of the high percentage spirit absolutely essential for dehydration, cannot be accomplished by simple distillation, but only by using a rectifying apparatus. In the laboratory the lime method must be used. On the other hand, acetone, miscible with water, is at the same time, an excellent fat solvent. It can be recovered from its aqueous solutions by a simple distillation in a state in which it may be immediately reused for dehydration and removal of fats. Thus the removal of water and fats from albuminous materials is accomplished, according to him, by placing freshly precipitated and filtered casein, for example, in an extraction apparatus in which the casein is extracted with acetone, either hot

[13] Argutinski, P., *Pflüger's Arch. Physiol.*, **55**, 351 (1894).

[14] Viss, G. N., German patent 98911 (1897); *Chem. Zentr.*, **69**$_{II}$, 1231 (1898).

or cold, until a sample is free from fat, and shows only a small water content. Those who, like the writer, have often sought to remove the water and fats from freshly precipitated casein with alcohol and ether, by the older methods, will appreciate the value of the improvement. In conclusion, it may be mentioned that carbon bisulfide gives particularly high values in quantitative fat extractions, the reason being that it also extracts any rancid fat present.

EXTRACTION WITH LIQUEFIED GASES

Friedrichs[15] discusses extraction with liquid gases as follows: In choosing a solvent for an extraction, the solubility of the material to be separated is of prime importance. In the second place, care must be taken that the solvent may later be removed easily and without loss, as well as without decomposition of the extract or of the residue. The lower the decomposition temperature and the higher the vapor pressure of the material being heated, the lower should be the boiling point of the solvent chosen, since it is usually removed by evaporation. This logically leads to the use of liquefied gases as extraction media, if the usual solventscannot be recovered after the extraction without loss or decomposition of the extract.

Friedrichs believes that the cheap liquefied gases such as ammonia, sulfur dioxide, hydrogen sulfide, methylamine, etc., have been used so infrequently because their solvent power has been little investigated, and because the older types of extraction apparatus,[16] although devised for this purpose, are not very convenient. His apparatus (fig. 102) consists of 3 parts, the extraction apparatus proper, the container for the material to be extracted hanging in this, and the ground-in condenser. The flask *F* of the extraction apparatus is provided with a small syphon and a cock *G* for drawing off the extract, and the whole apparatus is insulated by a vacuum jacket. A little of the cooling agent may be placed between this vacuum jacket and the extraction apparatus. The screw shaped vessel *A* of the condenser[17] contains the cooling agent. It, like the extraction apparatus, is surrounded with a vacuum jacket, and to permit a free outflow of the condensate, it is provided with separate vapor and liquid leads shown in the figure. It is necessary to make elastic all the connections which pass through the vaccum jacket, to avoid breakage of the apparatus due to expansion or contraction. The upper tubulure of the condenser admits the gas and is connected with a mercury manometer, which also acts as a safety valve, with a suitable drying train (for ammonia a long tube containing sodium wire), and with the gas supply, a bomb or gas generator. The gases listed above are best cooled with solid carbon dioxide and ether, while liquid air is used for such gases as oxygen or methane. When using liquid air, it is well, in order to avoid breaking the apparatus, first to put in some ether and then slowly add the liquid air. Instead of allowing the cooling agent to boil under atmospheric pressure, still lower temperatures may be reached by connecting the screw vessel with an air pump, and drawing off the evaporating liquefied gas.

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[15] Friedrichs, F., *Zeit. f. angew. Ch.*, **26**, 201 (1913).

[16] Browne, A. W., and Houlehan, A., *J. Am. C. S.*, **33**, 1735 (1911).

[17] Friedrichs, F., *Zeit. f. angew. Ch.*, **23**, 2425 (1910).

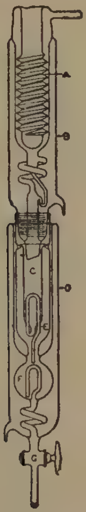

FIG. 102. EXTRACTION WITH LIQUEFIED GASES (FRIEDRICHS)

EXTRACTION OF LIQUIDS

Under the heading "Extraction", reference was made to the fact that the extraction of liquids is a substitute for working with a separatory funnel, and is particularly important for the quantitative extraction of small quantities of liquids. Only the apparatus which is to be described last is suitable for larger volumes of liquids. The number of types of apparatus devised for this purpose is legion. The following ones will suffice for all purposes, especially the last one which is arranged for working under the most adverse circumstances.

The apparatus designed by Schwartz will be considered first. It may be assembled easily by any one. The extraction liquid, ether, for example, which is lighter than water, is boiled in the flask A (fig. 103). Its vapor passes through B to the pre-cooler C, which has a special form and is connected with the real condenser D. The condensed ether runs from the pre-cooler C, through a tube E, ending below the liquid to be extracted in the round flask F, whose side tube returns the ether into A. The cycle is then repeated. If still smaller quantities of liquid are to be extracted quantitatively, van

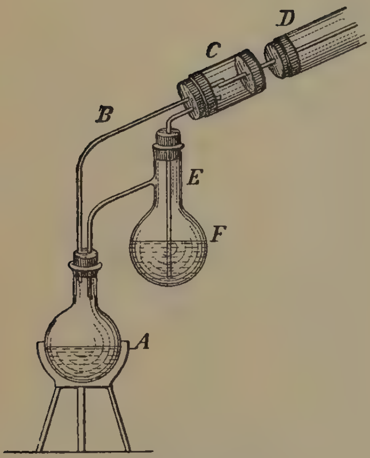

Fig. 103. Extraction Apparatus (Schwartz)

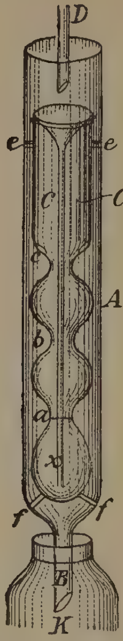

Fig. 104. Extraction Apparatus (van Rijn)

Rijn's[18] apparatus may be used (fig. 104). It is so arranged that weighing the liquid to be extracted may be eliminated by making a simple measurement of its volume instead. It consists of a wide glass tube A, ending below in a smaller tube B and a tube C, which is constricted at a, b and c and has four holes of equal size at c. At the constriction a, there is a mark denoting exactly 20 cc. for the lower chamber. The tube C is supported in the tube A by the glass projections e and f. A funnel tube is hung in the tube C and extends almost to the bottom. The action of the apparatus may now be easily understood. The liquid to be extracted is put into the chamber x by means of a pipette or through the funnel tube. The ether vapors ascending from K pass through B, heat the space x, pass on around e into the condenser D. The drops of ether fall back into the funnel tube, go through the liquid in x, become saturated there with alkaloid, fat, etc., and rise around the funnel tube and fall back, through the holes at c, into the flask K. After the extraction, the ether is evaporated from the flask and the residue dehydrated in a drying oven or desiccator. The quantity of material recovered by extraction from the sample of liquid taken, may be determined from the increase of the weight of the flask, which had been weighed empty. This very convenient apparatus for extraction media, lighter than water, was further developed by Winter and Baum[19] who devised a similar, simple apparatus for heavier extraction media (fig. 105). The extraction tube about 3 cm. wide, is placed in a long adapter and has a small tube bent upward and about the same width as the syphon tube of the Soxhlet apparatus sealed in to its lower end to serve as an overflow for the extraction medium. It is about one-third the length of the extraction tube. The lower end of the adapter is connected with the flask in which the extraction medium, such as chloroform, etc., is to be boiled, and is fitted to the condenser above. The extraction tube is first charged with some chloroform, and the liquid to be extracted poured over this, forming a separate layer. The chloroform returning from the condenser sinks through the liquid, extracts it, reaches the bottom, rises in the overflow tube, runs over, and returns to the flask.

[18] Van Rijn, J. J. L., *Ber.*, **28**, 2387 (1895).

[19] Baum, E., *Ch. Zt.*, **28**, 1172 (1904); Winter, H., *Ch. Zt.*, **28**, 1271 (1904); Kempf, R., *Ch. Zt.*, **34**, 1365 (1910); Tolmacz, B., *Ch. Zt.*, **37**, 1381 (1913); Zelmanowitz, C., *Bioch. Zeit.*, **1**, 253 (1906); Kutscher, F., and Stendel, H., *Zeit. physiol. Ch.*, **39**, 475 (1903).

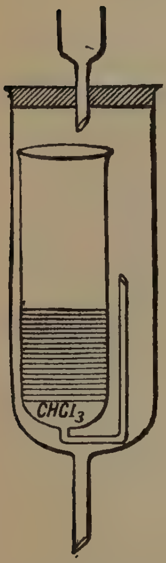

Fig. 105. Extraction-Apparatus (Winter and Baum)

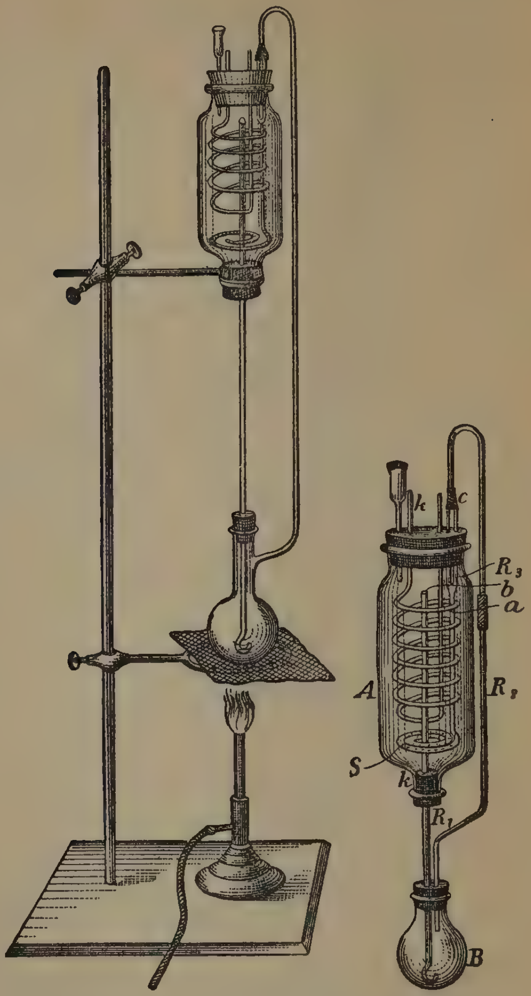

Fig. 106. Apparatus for the Extraction of Liquids by Means of Ether, Chloroform, etc., and Method of Fastening to Stand (Hagemann)

Other similar devices have been constructed by Neumann,[20] Tscherniac,[21] Pregl,[22] and Hagemann,[23] etc. In Hagemann's apparatus (fig. 106), the liquid to be extracted is placed in the container *A*, filling it, for instance, to the level *a*. The extraction medium (ordinarily ether) is placed in the flask *B* and is boiled on a water bath. Its vapors pass through R_2 into a glass spiral S_1, open above and having many fine openings along its side from which the vapors, in a very fine state of division, enter the liquid to be extracted; they condense and slowly rise in the form of innumerable small droplets. A layer of ether gradually collects above, and as soon as this reaches the height *b*, it automatically runs back through the tube R_1 into the flask *B*. To prevent the liquid in *A* being heated to the boiling point of ether—this would result in violent upheaval of the whole mass so that aqueous liquid as well as ether solution would reach the flask *B*—a cooling coil *k*, of about the form shown, is essential. Experience has shown that an extra condensing contrivance for any ether which may escape is entirely superfluous, since the extraction vessel *A* may be closed tightly enough, though not hermetically, by a cork, to prevent too much air circulation, and consequently, the loss through evaporation of ether is a minimum. A uniform, quiet boiling of the ether in *B* is necessary for the proper functioning of the apparatus, as Tscherniac, especially, has pointed out. If the boiling is spasmodic, the pressure in the boiling flask may become too great to be equalized by the fine openings of the spiral, and as a consequence, the ether will be flung through the tube *R*, into the vessel *A*, and although it will return later, this occurrence retards a uniform rapid extraction. According to Hagemann such uniform boiling is easily attained by adding several pieces of unglazed, porous plate of the ether, and the writer also found this satisfactory. Others use two glass beads.

If the extraction is proceeding properly, a column of ether forms in the tube R_1, of such a height that it corresponds to the hydrostatic pressure of the liquid in *A*. Since the tube R_1 may be moved in the cork *k*, it may be placed at any desired height, and thus be adjusted for any quantity of liquid. The corresponding movement of the tube R_2 takes place at *c*, where it is pushed into the somewhat wider spiral adapter R_3. The joint is made tight by a piece of soft rubber tubing drawn over it, which is chosen of just such a width that the tube R_2 can still be easily moved. The rubber may be closed off from the ether vapors, though this is usually not necessary, by placing between the two walls of the tube, a drop of water which is held in place by capillarity. This keeps the ether vapors from reaching the rubber. It is well, for the sake of increased mobility, to divide the tube R_2 at another place and to use there a similar connection.

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[20] Neumann, G., *Ber.*, **18**, 3061 (1885).

[21] Tscherniac, J., *Ber.*, **25**, 3651 (1892).

[22] Pregl, F., *Z. anal. Ch.*, **40**, 785 (1901).

[23] Hagemann, C. Th. L., *Ber.*, **26**, 1975 (1893).

With slight modification, it is possible to make this apparatus serve for extraction media specifically heavier than the liquid to be extracted. To do this, the spiral *S* is placed in the upper part of the liquid, a spiral condenser placed above, and over the outlet tube R_1 is pushed a second wider tube, open top and bottom. Some extraction medium, chloroform, for example, is put in the bottom of *A*, before charging the whole apparatus. In this case, the chloroform vapors are first thrown upward and then fall to the bottom as condensed droplets. The liquid collecting below, rises between the outer and inner tube, and then flows, if R_1 has been set correctly, back into the boiling vessel.

Stephani and Böcker[24] constructed the following apparatus, when they were frequently obliged to recover compounds very soluble in water from strong lyes or very concentrated salt solutions, by shaking them out with chloroform. They often encountered all sorts of difficulties, such as emulsions hard to separate, or salts crystallizing out, etc.; in short, so many disagreeable things occurred that they took the trouble to assemble an extraction apparatus which accomplished not only cleaner, but more rapid and better results than any apparatus known up to 1902. The apparatus, which has been well tested, is in principle a separatory funnel in which the single parts are arranged in the proper order, and may be used for (1) the extraction of liquids with specifically heavier extraction media; (2) for the extraction of solids with any desired extraction medium. It may be used for any desired quantity of substance without diminishing its efficiency, according to the choice of the vessel *A*.

For the first case, the cock *g* is closed and the extraction medium is added through the filling funnel *H* to the level *a* and the solution to be extracted placed above this as far as *b* (fig. 107). The boiling vessel *D* is filled with the extraction medium, to about the height *c*. When the liquid in *D* boils, the vapors pass through *F*, F_1 and F_2 into the condenser *S*, where they are condensed and then divided by the distributor *V* (whose cross section is also shown in figure 107). To obtain continuous extraction it is only necessary to set the cock *g* so that the in- and outflow are equal. This is easily done. A little glass wool may be placed in the narrow neck of *A* to break up any emulsions that may form. The cooling coil *G* protects the liquid to be extracted from being warmed by the extraction medium, and at the same time, prevents loss of the latter.

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[24] Stephani, O., and Böcker, Th., *Ber.*, **35**, 2698 (1902).

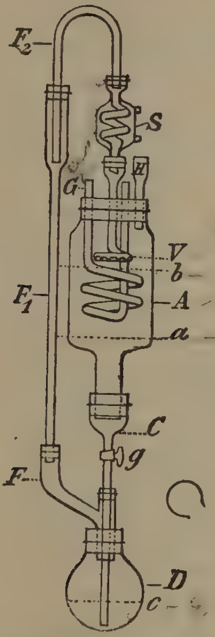

FIG. 107. UNIVERSAL EXTRACTION APPARATUS (STEPHANI AND BÖCKER)

If the apparatus is used for the extraction of solids, a purpose for which the inventors claim it is useful, the cooling coil *G* is removed, the solid added, (to the height *b*) and covered with several layers of filter paper to insure uniform distribution of the solvent. In this case, it is essential that glass wool be put in the narrow neck of *A* to avoid the loss of solid particles. The extraction may be conducted so that the substance is completely immersed in the extraction medium, or the latter may percolate through it. In the first case, the cock is set so that after the substance is thoroughly moistened, the quantities of liquid entering and running off remain equal; and in the second case, the cock *g* is opened wide.

When using extraction media that pass through cork easily, instead of the tube *C* carrying the stop cock, there may be placed in the narrow neck of *A* an outlet cock, having a bulb blown in its upper end, in such a position that the end extending into the vessel has its opening about 1 cm. above the cork. Small quantities of mercury or other suitable material will then protect it from contact with the extraction medium. If it is necessary to use a high boiling extraction medium or one which easily condenses, a jacket, which may be heated by steam, can be pushed over *F*. Various parts of this apparatus are best connected tightly with good corks, since on the one hand, they are easily replaced when no longer usable, and on the other, they permit the easy renewal of the glass parts that have become damaged. They may be covered with tin foil as proposed by Stanek. Finally, it may be stated, that in this apparatus the extraction medium may be completely run off and more added without removing the material being extracted.

CHAPTER XI

FILTERING AND PRESSING OUT PRECIPITATES

Filter papers are well known from inorganic work. Since 1916, there has also been prepared filter paper containing purified kieselguhr. This paper will retain the finest precipitates, such as barium sulfate[1] precipitated in the cold, etc. It is suited for the clear filtration of fats, etc.

As a rule, the methods of filtering used in inorganic work may be applied. However, those employed while making inorganic preparations,[2] are much inferior to those followed in analytical work. In organic chemistry, the opposite is true, and procedures for preparative purposes have gradually developed further. Liquids that contain finely divided precipitates that settle very slowly, and consequently can hardly be filtered, are put into centrifuges, which for this purpose, usually carry 6 glass containers of 250 cc. each. At 3000 revolutions per minute, in 0.5 hour at most, the precipitate will adhere so firmly to the bottom, that the clear supernatant liquid can be poured off.

The gel filtration devised by Bechhold[3] is an entirely new type. For this purpose, crude filter paper is impregnated with glacial acetic acid-collodion, for example, and this is then gelatinized by immersion in water. The original paper should be consulted for the further procedure, since this filtration is only rarely used in pure chemical work. Its efficiency, however, may be judged from the fact that at about 5 atmospheres pure water may be filtered from a solution of hemoglobin or of litmus in water, so in this way, it is possible to concentrate solutions that are on the filter. Further, it was possible to retain the chlorophyll from a technical chlorophyll solution in alcohol, which, in addition to chlorophyll, chiefly contained fats, waxes, etc., while the fats, etc., passed through the filter. This method of filtering has been greatly improved by the bacteriologists.

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[1] Grossfeld, J., *Z. angew. Ch.*, **29**, 364 (1916).

[2] Mach, F., and Lederle, P., *Ch. Zt.*, **41**, 521 (1917).

[3] Bechhold, H., *Z. f. Chemie u. Ind. d. Kolloide*, **2**, 3 (1907).

SYPHONING AND DECANTING

Attempts are usually made to syphon off larger volumes of clear liquid standing above poorly filtering precipitates and to wash the precipitates by decantation, before bringing them on the filter. However, ordinary syphons having both ends opening downward, exert a decided suction, and if it is desired to draw off the liquid from the sediment as completely as possible, a part of the precipitate is usually carried along. If the shorter end of the syphon is turned up (fig. 108), this disagreeable feature is eliminated. Indeed, the bent portion may be carefully placed in the precipitate, so that the opening *A* lies just above it, and yet, experience has shown, there is no danger of carrying away the precipitate.

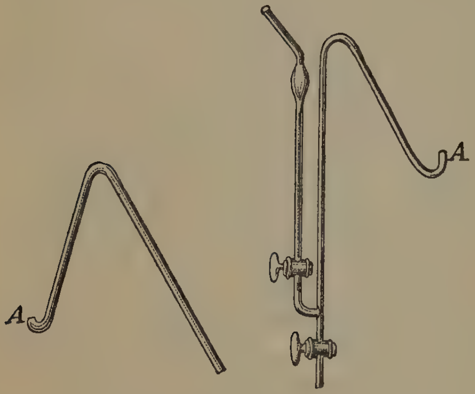

FIG. 108. SYPHONS WITH UPTURNED ENDS

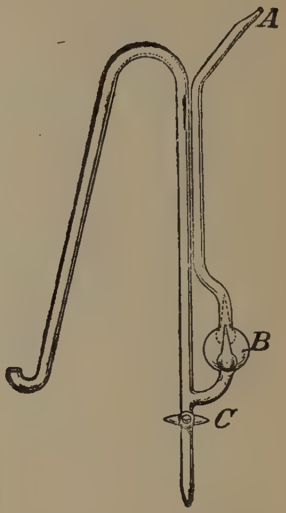

FIG. 109. SAFETY SYPHON

Suitable for the separation of small amounts of liquids (Matton).

Matton[4] found that none of the syphons devised up to 1910 would separate very small volumes of liquid and yet insure against more than one of the layers being sucked over. Both of these requirements are met by his device reproduced here (fig. 109). If suction is applied at *A*, the liquid rises until the float in the bulb *B* fits into the suction tube with an audible click, and prevents further suction. If, however, when dealing with small quantities of liquid, both liquids enter the syphon when sucking, they may still be separated from each other, drop by drop, by carefully opening the cock *C*.

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[4] Matton, K., *Z. angew. Ch.*, **23**, 20 (1910).

FUNNELS, FOLDED FILTERS, RIBBED FUNNELS

Instead of placing paper filters in ordinary funnels, a glass ball may be laid in them and a layer of sea sand, 1 to 2 cm. high, placed on it. Filtration usually proceeds rapidly, and if the filter clogs, the top layer of the sand may be carefully scratched away with a spatula, even though the funnel is full, and the filtration thus speeded up again. Most of the substance can be removed from the funnel, free of sand, and the rest is separated from it by floatation. In dealing with a comparatively coarse grained material, such as crystals in their mother liquor, the sand may be omitted.

It is often necessary to use folded filters. When filtering hot, saturated solutions, the folded filter is placed in a funnel without a neck. In this way, the disagreeable clogging of the entirely superfluous neck, that results from the separation of the crystals, is avoided. Instead of a hot water funnel, a short funnel without a neck may be set upon a beaker of suitable size, and it, together with the liquid to be filtered, placed in a drying oven and heated to the proper temperature (fig. 110).[5]

Folded filters are inconvenient to prepare and tear easily. In their place, it is better to use ribbed funnels in which smooth filters are laid. The form of the funnel is such that half of the surface is active for filtration. Of the glass ribbed funnels, the writer has found the form shown in *A* (fig. 111) to be the most rapid; but the porcelain funnel *B* has given good service. Since the latter store up considerable heat they remain hot for a long time and may often save the use of a hot water funnel for rapidly-filtering liquids. As soon as large funnels are used there is always danger that the point of the filter paper will tear, because of the excessive pressure of the column of liquid resting on it. This may be avoided by putting a small ordinary funnel in the opening of a large ribbed funnel to give the point the necessary support.

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[5] The filtration of hot, saturated solutions in volatile solvents such as alcohol or benzene is often satisfactorily accomplished by pouring the liquor through a folded filter on a funnel stoppered to a flask in which the filtrate is boiling just vigorously enough to surround the paper with solvent vapor. (See footnote 10, Chapter X.)—H. T. C.

Schmatolla[6] has devised a control glass which permits the examination, at any time, of the filtration of a liquid as to clarity, color and rapidity, without interrupting the work or taking a sample (fig. 112). When in use, the inlet of the glass is connected with the outlet of the funnel so that the filtrate passes through the tube.

FILTRATION BY REDUCED PRESSURE

Filtering by the aid of reduced pressure to accelerate the process, and for more convenient handling of the precipitate, has also led to many modifications of the methods used with inorganic precipitates for analytical purposes. However, the principle itself can undergo no changes. Schmidt[7] used a suction pump when filtering through cloth an ether solution saturated with nitrous vapors. In organic work it is often of great value to recover even small quantities of filtrate with the smallest possible loss. Receivers having the form and size of test tubes and held on supports by springs, are now available (fig. 113). In these, in contrast to the usual large filter flasks, little of the liquid remains behind. In the older filter flask

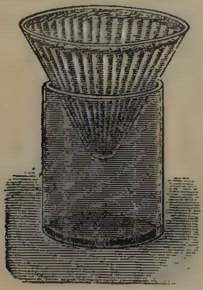

FIG. 110. FUNNEL WITHOUT STEM WITH PLEATED FILTER FOR THE FILTRATION OF HOT LIQUIDS DIRECT INTO BEAKER

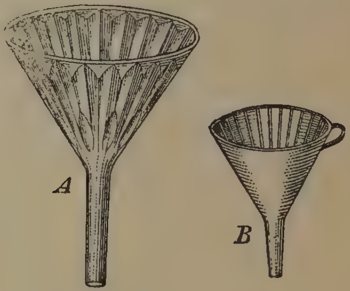

FIG. 111. RIBBED FUNNELS

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[6] Schmatolla, O. K., *Ch. Zt.*, **32**, 758 (1908).

[7] Schmidt, Julius, *Ber.*, **34**, 621 (1901).

the neck of the funnel had to pass through a rubber stopper, which in its turn had to fit the neck of the flask. Walter makes an air tight seal by having the neck of the receiver in the form of a funnel (fig. 114). If a rubber ring *A* of the proper size, is placed in this, any funnel may be set in it directly, and the joint automatically becomes tight because of the air pressure, as soon as the pump is turned on. It is not necessary to press the rubber stopper into the neck of a receiver, and what is more important, after the pump is turned off, the filled funnel may be lifted from the receiver without having to pull it, which often causes part of the contents of the funnel to be thrown out. According to Erlenmeyer,[8] rubber stoppers may be successfully replaced in vacuum filtrations, by rubber caps such as are found on the market for closing icebags. It is only necessary to cut a circular hole with a cork borer, and they are then slipped over the suction flask. Funnels of all kinds, even Gooch crucibles, may be easily placed in the hole of such a rubber cap. When the air pump is turned on, the rubber forms a tight seal all around.

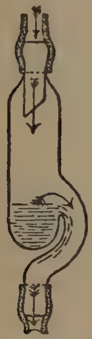

FIG. 112. FILTER CONTROL (SCHMATOLLA)

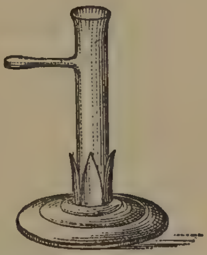

FIG. 113. FILTERING FLASK (TEST-TUBE FORM)

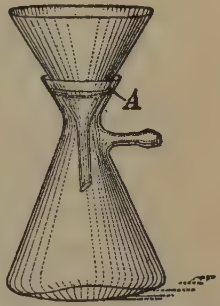

FIG. 114. FILTERING FLASK WITH FUNNEL-SHAPED NECK (WALTER)

To prevent the material collecting on the filter from being drawn into the point of the funnel, and to enlarge the filtering surface, which always hastens filtration, Witt[9] has proposed that porcelain filter plates with many perforations (fig. 115) be placed in the funnel.

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[8] Reis, F., *Ch. Zt.*, **28,** 852 (1904).

[9] Witt, Otto N., *Ber.*, **19,** 918 (1886).

These are covered with an ordinary round filter paper. Buchner[10] had the plate and the funnel made of one piece of porcelain. While the Witt plates in glass funnels are excellent for small quantities of material, the writer prefers the Buchner device, which is always tight for larger quantities. Figure 116 shows a filtering funnel of this type with straight sides. Since the mass of porcelain is rather large, it is a good heat reservoir. If a funnel of this kind is placed for some time in a hot water bath or in a warming oven, it may be used as a sort of hot water funnel for filtering quantities not too large.[11]

The product "sucked down" may be tamped, if necessary, with more or less success, with ordinary porcelain pestles, glass stoppers, small bottles, or even with the bases of measuring cylinders.[12] All of these are not only hard to handle, but are also fragile, so that the product may be contaminated by glass splinters. Michaelis[13] has devised a tamp in the form of a flattened pestle. The bottom is an oval (10 to 12 cm. in diameter) to fit the edge of the filter.

The Buchner funnel is shown on a receiver fitted with a stop cock, as proposed by Wahl.[14] The advantage of this cock is as follows: When filtering by the usual method, as long as the filtration continues, the pump must constantly maintain the vacuum, consequently, it cannot be used for another filtration at the same time. When this cock is included in the apparatus, it may be closed as soon as the receiver has been evacuated, and the filter pump is then available for other purposes. Reliable methods of sealing such cocks were discussed in the chapter on "Distillation." A glass tube closed at one end may be placed in the flask. This remains empty as long as the vacuum is maintained, but fills with the filtrate as soon as a trace of air enters. Porcelain funnels of the usual form fitted with Witt plates, recommended by Hirsch, have given good service.

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[10] Buchner, E., *Ch. Zt.*, **12**, 1277 (1888).

[11] Buchner funnels have been found suitable for the filtration by gravity of liquids containing slimy precipitates which clog the paper when employing suction. The flat paper and cylindrical sides of the funnel permit the solids to collect in a compact form which can be washed more readily than in a conical funnel. The first runnings are collected separately, as they are usually turbid; when the filtrate runs clear the receiver is changed and the cloudy liquid returned to the funnel. Subsequent additions can be made without disturbing the clarity of the filtrate. Such filtrations are necessarily slow, but incomparably more rapid than would be the case were suction applied.—H. T. C.

[12] Gortner, *J. Amer. Chem. Soc.*, **36**, 1967 (1914), has proposed the use of a thin indiarubber sheet to assist in freeing solids of liquid. The sheet is placed on the wide end of the funnel so that when suction is applied it is drawn down onto the precipitate and exerts thereon a pressure nearly equal to that of the atmosphere. The precipitate may then be tamped through the sheet. This simple and efficacious method is greatly to be recommended, not only for finely divided precipitates, but for crystals of the needle type from which liquid is not readily removed by suction in the ordinary way.—H. T. C.

[13] Michaelis, P., *Ch. Zt.*, **46**, 225 (1922).

[14] Wahl, A. R., *Ch. Zt.*, **21**, 415 (1897).

In 1905, Buddëus proposed that the Witt plates which still require a covering layer of filter paper or asbestos, be replaced by filtering plates of acid and alkali-resistant filtering stone, fitted with an asbestos ring (fig. 117). These plates are said to have an almost unlimited life since they are not attacked by hot or cold acids, alkalies, strong oxidizing or corrosive liquids. It is claimed that they practically never clog. Porous stone filtering plates such as are used, for example, in place of the gravel formerly used for filtering the arsenic sulfide obtained when freeing sulfuric acid from arsenic, require no cleaning after years of use.[15] The plates may be cleaned, if necessary, by brushing the surface with water. In case they should become contaminated by organic materials insoluble in all solvents, they may even be gently ignited without losing any of their efficiency. The inventor claims that all possible filtrations may be accomplished with one plate. Nitro products, dissolved alkali melts, chromate and

FIG. 115. FILTER PLATE (WITT)

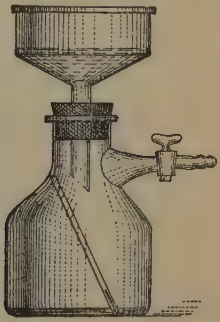

FIG. 116. FILTERING FLASK WITH STOP-COCK (BUCHNER AND WAHL)

permanganate oxidations, zinc chloride fusions, etc., no longer cause any difficulties when being filtered.[16]

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[15] S. Bornett & Co., Cologne, *Ch. Zt.*, **33**, 119 (1909).

If the filtrate is to be caught in a beaker instead of a filtering flask, a desiccator having a tubulure in the cover is used to hold the funnel with either a stopper or a ground glass joint to make the apparatus tight, the beaker being directly under the funnel (fig. 118).

When working with quantities larger than can be handled on the ordinary filters, another type of suction funnel which was also first recommended for laboratory practice by Buchner,[17] may be used. It is a large porcelain sieve (fig. 119) which is ground to fit a glass cylinder having two tubulures. The upper one is connected with the air pump, while the filtrate may be run off from time to time, through the lower one, after the pump has been turned off.

Pukall[18] attempted to solve, in an entirely different way, the problem of filtering under diminished pressure. His filters are not made of paper, but are hard burned porous clay flasks (fig. 120). The biscuit ware is so hard that their surfaces are not scratched by steel, which is abraded by them, so there is little danger of their breaking. The filtration takes place from the outside to the inside, as the filter *a* is placed in the beaker *d*. The connection with the receiver *c* is made through the glass tube *b*, which is made flexible by a rubber connection. After the system has been evacuated, the cock *e* is closed and the apparatus allowed to stand over night. The filtration proceeds more rapidly or more slowly, according to the quantity of precipitate that adheres to the flask. The filtrate is always clear and it makes no difference whether the liquid is strongly acid or alkaline, or hot or cold. The precipitate is easily washed and is easily removed later, or may be rinsed off. A simplified form of

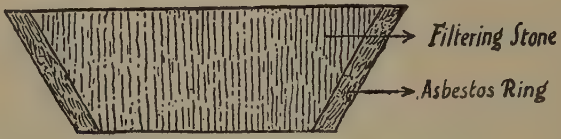

FIG. 117. STONE FILTER WITH ASBESTOS RING (BUDDÉUS)

these filters may be devised from ordinary funnels covered with silk or nitrated cotton and then hung upside down in the liquid.

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[16] Plates made of powdered glass sintered together are now permanently placed in glass funnels.—E. E. R.

[17] Buchner, E., *Ch. Zt.*, **13**, 95 (1889).

[18] Pukall, W., *Ber.*, **26**, 1159 (1893).

FILTRATION WITH EXCLUSION OF AIR

Frequently liquids must be filtered which are hygroscopic, or have other properties such that they should not come in contact with the open air. This is true, for instance, of the ether extracts of hygroscopic materials when being filtered from any drying agent, preparatory to evaporation. If this is done in the open air, the hygroscopic properties of the ether itself are sufficient to cause the attraction of considerable water. The apparatus of Pip[19] provides a remedy for this (fig. 121). The wide edge of the funnel is narrowed at the top so that it can be closed with a stopper. The opening is still wide enough to permit the easy introduction of a folded filter. If the neck of a separatory funnel containing the liquid to be filtered, together with any drying agent, is put through the stopper, it is possible by means of the cock to run the liquid on to the filter at any speed and thus accomplish the filtration with exclusion of the outer air. The long neck of the funnel permits the introduction of the filtrate into a fractionating flask and thus it is possible to continuously evaporate rather large quantities of extract to a small volume.

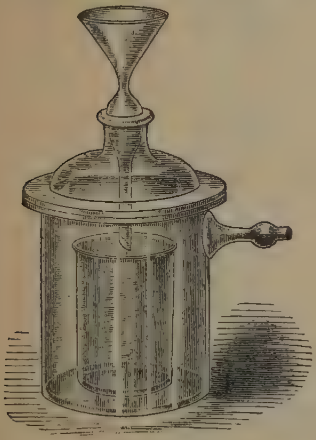

FIG. 118. COLLECTION OF FILTRATES IN BEAKER

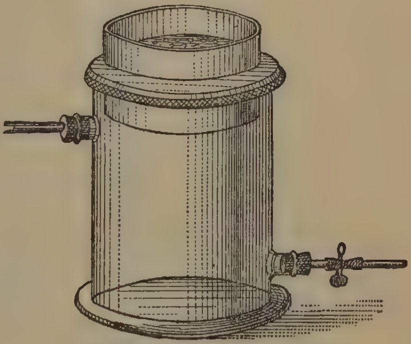

FIG. 119. SUCTION FILTER

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[19] Pip, W., *Ch. Zt.*, **28**, 818 (1904).

E. Fischer,[20] when preparing the hydrochloride of aminocaproic acid chloride, pure enough for analysis, had to filter the very spongy crystals of this material, which is extremely sensitive to moisture and elevated temperatures, in perfectly dry air, and then wash it with acetyl chloride and petroleum ether. He found that only the Pukall clay filters could be used (fig. 122). The reaction is carried out in a stoppered cylinder *a*. In this is the clay cylinder *b* into which the tube *c* reaching almost to the bottom, is fastened by a rubber stopper. A two-hole rubber stopper closes *a*, *c* passing

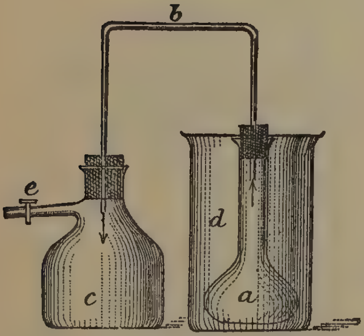

FIG. 120. CLAY FILTER FLASKS (PUKALL)

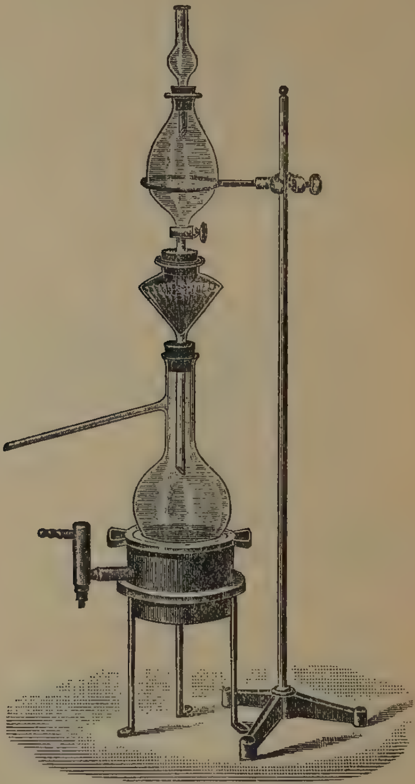

FIG. 121. FILTRATION WITH AIR EXCLUDED (PIP)

through one hole and the tube *d* through the other. This has two branches, *e* and *f*, each provided with a cock; *f* serves to remove the wash liquid from the bottle *g*, while *e* leads to the tower *h* filled with phosphoric anhydride and to the bottle *i* filled with sulfuric acid. These dry the entering current of air. The suction flask *l* is connected with *c* by the rubber tube *k*. If suction is applied at *l*, the liquid in the cylinder *a* passes through the clay cell and reaches *l* through the tube *c*. At the same time a slow, dry current of air enters the vessel through *e*. Most of the precipitate adheres firmly to the clay cell. The washing is accomplished by closing the cock at *e* and opening the one at *f*, and the wash liquid will then pass from *g* to *a*. Fresh acetyl chloride is placed in *g* which is later replaced by another vessel containing petroleum ether dried over phosphorus pentoxide. To facilitate the influx of the wash liquid it is well to momentarily cool the cylinder *a* in which there is only a slightly reduced pressure because of the high vapor tension of the liquids used, by placing it in a freezing mixture or by spraying ether upon it. The operation is still more convenient if the cylinder *a* is connected with a third tube, not shown in the figure, carrying a stop cock and which may be directly connected with the suction pump. One washing with as much acetyl chloride as filled the cylinder *a* to the height of the precipitate and two washings with the same volume of petroleum ether were sufficient to produce a preparation pure enough for analysis. The precipitate was finally sucked as dry as possible

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[20] Fischer, Emil, *Ber.*, **38**, 616 (1905).

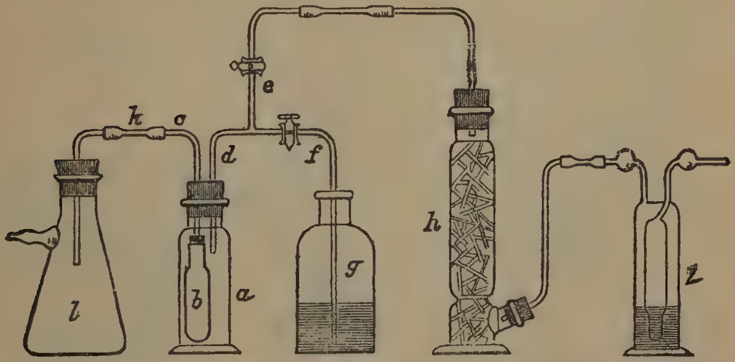

FIG. 122. FILTRATION AND WASHING OF PRECIPITATE WITH OPTIONAL MEDIA IN DRY AIR (FISCHER)

in a current of dry air, and then transferred as rapidly as possible to a vacuum desiccator charged with phosphorus pentoxide, and dried for about 1 hour to remove the last portions of the petroleum ether.

HOT WATER AND HOT VAPOR FUNNELS

Hot funnels must be used for hot saturated liquids from which crystals begin to separate while cooling, since otherwise the cooling starts the crystallization in the funnel, and makes further filtration impossible. If the volume of the liquid to be filtered boiling hot is small, as is usually the case with materials designed for ultimate analysis, a heated funnel (without a neck) containing a folded filter (fig. 110) may be used. A well heated procelain filtering funnel (see above) is usually satisfactory for somewhat larger quantities. In special cases, hot water funnels of the type shown in figure 123 may be used. Frequently, however, the solutions to be filtered are inflammable, and consequently hot water funnels have often caused

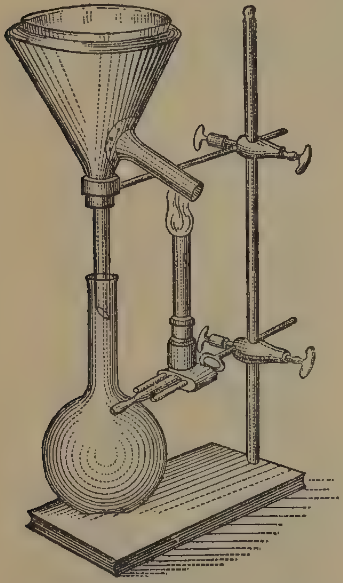

Fig. 123. Hot Water Funnel

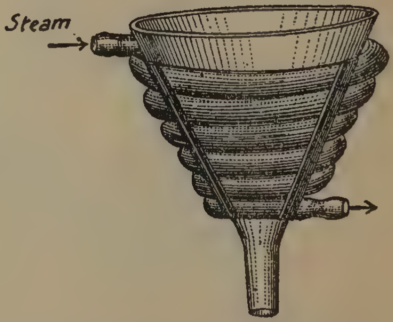

Fig. 124. Hot Vapor Funnel (Bergami)

small fires in laboratories because of flames near them. Consequently in such cases, it is better to use the hot vapor funnels of Bergami and Stange (fig. 124). They are heated by a current of vapor passed through them, so there is no danger of fire. However, if the vapor funnel is to fulfil its purpose well, the temperature of the vapor must be considerably higher than that of the solution to be filtered. Cumol, boiling at 165°, is suited for aqueous solutions, while α-bromonaphthalene, boiling point 280°, may be used for aniline, phenol or nitrobenzene solutions.

The necessity of using such liquids which are not as plentiful as water has made it desirable to combine the vapor generator with the vapor funnel, so that the condensed vapor will flow back into the generator. Figure 125 shows Paul's[21] device for accomplishing this. The heating liquid whose boiling point may be as high as desired, is boiled in the copper vessel *S* by the burner *H*. The vapors rise through the tube *A* into the funnel shaped spiral *J*, circulate around the funnel, and return to *S*, which is fitted with a glass tube *D* about 60 cm. long acting as an air condenser. The shield *K* separates the burner from the filtrate. The tubulure *F* is used when filling and emptying the boiling vessel. Since there is a continuous return of the

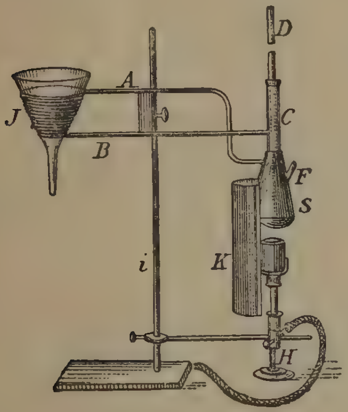

FIG. 125. HOT VAPOR FUNNEL FOR HIGH TEMPERATURES (PAUL)

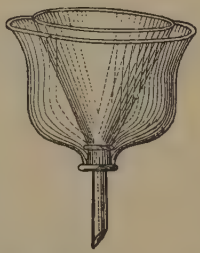

FIG. 126. ICE FUNNEL (SCHMIDT)

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[21] Paul, Th., *Ber.*, **25**, 2209 (1892).

liquid, the apparatus may be kept in action indefinitely with 30 to 50 cc. of the boiling liquid. There are also available suitably arranged double funnels made of glass, fitted with supply and exit arms. These glass funnels are cleaner.

It often happens that even when hot water or hot vapor funnels are used, the filtration does not proceed rapidly enough since the filter finally clogs. In such cases, nothing more can be done than to cover the filter well, and place it, together with a support, in a warming closet heated to the proper temperature, and thus give the liquid sufficient time to run off. Special apparatus designed for this purpose for chemical laboratories is not available. The vapor sterilizers commonly used in bacteriological work which might be used, are suitable only for aqueous solutions.

ICE FUNNELS

If it is necessary to filter blood or similar liquids that decompose easily, the funnel may be surrounded by a cooling jar as recommended by Schmidt (fig. 126). This is filled with ice or a freezing mixture.

PAPER, GLASS WOOL, NITRATED COTTON, AND ASBESTOS FILTERS

Paper filters should always be used if possible, but there are various times when their use is not advisable. This is true when studying albumins. For instance, many albumin precipitates, after being washed thoroughly, adhere so firmly to the paper that they cannot be obtained free from paper fibers, and are then no longer suited for ultimate analysis.[22] In such cases, in place of the paper, circular pieces of fine white silk,[23] folded like paper filters, may be placed in the funnel. Although the nature of the precipitate itself may be the reason for not being able to use paper filters, this is much more often due to the too acid or too alkaline nature of the material to be filtered. It may be noted that alkaline liquids which should not be filtered through paper, may often, if not too alkaline, be filtered very well through cotton.

Up to a few years ago, in scientific laboratories, only the use of glass wool or asbestos for special cases was known, the glass wool being the more rapid. Nitrated cotton fabric has been found well suited for liquids containing acid and chlorine. It was recommended for this purpose as early as 1892 by Hering.[24] It is prepared, according to Claessen,[25] by immersing the cotton fabric for an hour in cold nitric acid (40 to 50°Bé.) and after the adhering nitric acid has drained off, for another hour in sulfuric acid (60°Bé), and then thoroughly washed with water; cellulose pentanitrate results. The Dye Works, Friedr. Bayer and Company,[26] state that if the nitration is properly conducted, the tearing strength is not lessened. This cloth whose ignition point is 170°, is very resistant to concentrated acid and to chlorine solutions at temperatures up to 50°. Claessen states that filter cloths designed to withstand the strongest acids should be woven from threads which have been made of nitrated cellulose dissolved in ether-alcohol. The experience of Bayer and Company, does not substantiate this. Such cloth is dissolved much more readily by concentrated sulfuric acid, is less resistant to chlorine, very porous and has low tensile strength.

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[22] It is advisable to employ hardened filter papers whenever collecting crystals destined for analysis.—H. T. C.

[23] Bondzynski, S., and Zoja, L., *Z. physiol. Ch.*, **19**, 8 (1894).

Berzelius[27] introduced asbestos as a filtering material. If untreated, crude asbestos is put into a funnel, the filtration is usually very slow. The preparation of a good filtering asbestos is by no means as simple as is usually assumed, but, according to Casamayor,[28] it should be prepared as follows: The asbestos is rubbed through a coarse sieve, the part passing through then separated from the finest particles on a fine sieve, by a stream of water, the residual suspension of asbestos extracted in a beaker with hot concentrated hydrochloric acid, washed with water in a funnel fitted with a perforated platinum cone, and after drying, ignited in a porcelain crucible.

Windisch[29] states that commercial asbestos contains up to 11 per cent of material soluble even in hot water, which is said to consist principally of hydrated magnesium and calcium silicates. According to Bernhardt,[30] suitable asbestos is obtained by the following procedure: Good, pure asbestos in large quantities, if desired, is freed of all organic impurities by careful ignition, extracted twice with hot, dilute soda lye; the lye removed by several boilings with water; then extracted twice with hot dilute nitric acid; the nitric acid removed by repeated boilings with water, and then dried in thin layers at about 110°.

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[24] Hering, O., German patent 72969 (1892) *Ber.*, **27**, R, 324 (1894).

[25] Claessen, C., *Z. angew. Ch.*, **20**, 316 (1907).

[26] Farbf. v. Fried. Bayer &Co., *Z. angew. Ch.*, **20**, 571 (1907).

[27] Berzelius, J. J., *Lehrbuch der Chemie, Dresden*, 1841, X, p. 264.

[28] Casamayor, P., *Chem. News*, **47**, 17 (1883).

[29] Windisch, K., *Wochenschr. f. Brauerei*, **22**, 48 (1905).

[30] Bernhardt, Paul, *Ch. Zt.*, **32**, 1227 (1908).

Lohse[31] who has written extensively concerning the history of asbestos filtration, recommends the use of asbestos filter tubes having the thickness of a combustion tube, and sealed round at one end which then is provided with a ring of openings (fig. 127). The other end is expanded. The tube is 12 cm. long, 15 mm. in diameter, and the diameter of the wide part is 20 mm. When filtering, he uses an adapter *A* such as is used for Gooch crucibles. He recommends that the suction flask be provided with a scale of volumes.

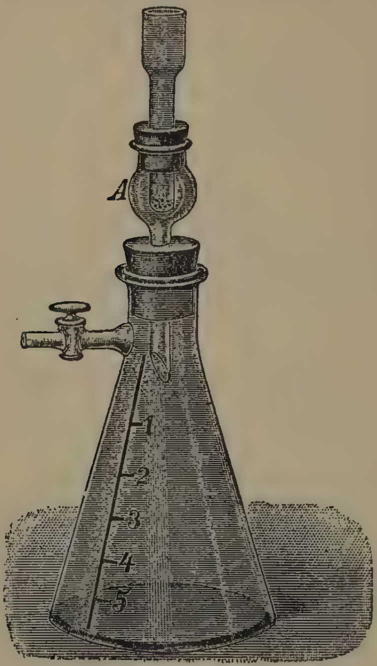

FIG. 127. ASBESTOS FILTER (LOHSE)

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[31] Lohse, O., *Ber.*, **32**, 2142 (1899).

PERCOLATION

In organic work, many precipitates are obtained in considerable quantities, which can neither be washed by decantation nor sucked dry by a pump. In such cases, the liquid is percolated, and this, according to Gentele[32] may be done as follows: Strong, tightly twisted hemp cords are sewn along the edges of squares of cloth so that there are two cords extending about 30 cm. beyond each corner. The corresponding filter frames are made from 4 strips of wood which are somewhat longer than the sides of the cloth. These strips are put together so that they form a rectangle, and at the four corners, crosses whose ends extend beyond the rectangle. When in use, the cloth is tied on by passing the cords around the crossings of the strips, and fastening them so that each corner of the cloth fits one corner of the frame. These frames are then placed on a support so that the filter cloth hangs free and a vessel placed underneath. When filtering, the cloths are first moistened which is best done before they are tied. This draws the meshes together and the precipitate does not run through so easily.

A vessel is placed under every cloth so that the point of the sack formed is above the vessel. The precipitate to be filtered is then put on the cloth which may be covered with filter paper, but since the paper is apt to float up, it is better to lay a second cloth above it. This latter method is also used in technical practice for perfectly clear filtration of boiling solutions. For this purpose, cloths 1 meter square are used, with suitable stretcher frames, the sheets of paper between the cloths extending beyond the edges to insure perfectly clear filtration The writer has often filtered 1000 liters of boiling potassium ferrocyanide solution in one and one-half hours, with three such filters.[33] The first runnings, which are rather turbid, are poured back until the filtrate is satisfactory. In the laboratory, the passage is accelerated by pushing the solid material from the outside toward the inside with a spatula, so that the liquid again comes in contact with the cloth. While doing this, the receiver is changed because the filtrate at first is slightly turbid. If filter cloths are to be kept for long periods, they must be well washed after each using.

[32] Gentele, J. G., *Farbenfabrikation*, Stuttgart, 1860.

[33] Lassar-Cohn. See the cut p. 341 of Volume VII of *Buches der Erfindungen, Gewerbe und Industrien*.

In factory practice, filter presses are commonly used. In the laboratory, the maximum force attained by reduction of the air pressure is 1 atmosphere, while in the factories, the material to be filtered is pressed between large filtering surfaces by pumps. Pressures as high as 20 atmospheres are used, but the difficulty of sealing the numerous chambers increases with rising pressure. The conditions are similar to those obtaining for autoclaves (see the heading "Sealed Tubes"). A chemist without technical experience cannot hope to accomplish the same results as a skilled factory worker, especially when the apparatus begins to need repairs. Filter presses for laboratory use have been constructed, but have not found favor for the reasons mentioned. The method of using them is apparent from their design.

WASHING PRECIPITATES

In practically all cases, precipitates suspended in aqueous liquids will be washed with distilled water; those in alcoholic ones with alcohol, etc. It should be mentioned that, when washing certain precipitates suspended in water, distilled water, unless absolutely necessary, may often be advantageously replaced by a weak salt solution, since this is less apt to carry fine precipitates through the filter. Thus von Baeyer[34] found that the hydrated manganese dioxide separating from an alkaline solution during an oxidation by potassium permanganate, passed through the percolation cloth when washed with distilled water. This stopped immediately when water containing sodium carbonate was used.[35] In inorganic chemistry we learn, for instance, that river water in which clay has been suspended, settles clear within a few hours, while if the same quantity of clay is stirred up with the same volume of distilled water, this will remain turbid for days; because the finest particles continue to oscillate there is nothing striking about the above phenomenon. A suspension of the finest ultramarine[36] acts similarly.

Ritthausen[37] states that gluten is obtained from wheat flour much more easily if the flour is made into a dough, not with 70 to 80 per cent of distilled water, but with this quantity of hard water, or of gypsum solution, because during the subsequent washing, the carbonates and sulfates dissolved in the water, hinder the solution and washing away of those constituents of the flour which give the gluten its characteristic nature.

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[34] Baeyer, A., *Ann.*, **245**, 138 (1888).

[35] The colloidal material is precipitated by the electrolyte but is dispersed again in pure water.—E. E. R.

[36] Feigensohn, M., *Ch. Zt.*, **29**, 785 (1905).

[37] Ritthausen, H., *Die Eiweisskörper der Getreidearten*, Bonn, 1872, p. 4.

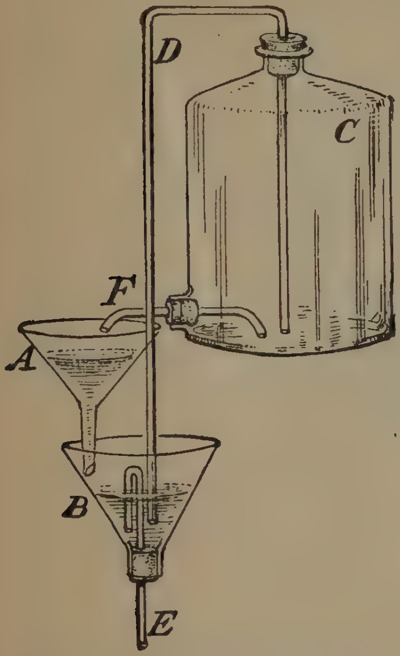

Fig. 128. Automatic Washing Apparatus (Grégoire)

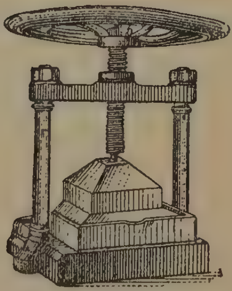

Fig. 129. Screw Press with Porcelain Jaws

Gregoire[38] has devised an apparatus for automatically washing precipitates (fig. 128). The precipitate to be washed is placed in the funnel *A*. The position of the syphon *E* in the lower funnel *B* regulates the flow of the wash liquid from *C*, since the filtrate will only flow from the funnel *B* after it has risen above the highest point of the syphon *E*. The syphon *D* now begins to function and delivers new wash water through the tube *F* into the funnel *A*.

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[38] Grégoire, A., *Bull soc. Ch. Belg.*, **24**, 223 (1910).

PRESSING OUT PRECIPITATES

It is often desired to free a precipitate that has been filtered with suction, or that has been well drained on a percolation cloth, of as much moisture as possible by pressing it out. Various types of presses were formerly used for this, but since they had metal cheeks they easily corroded. Witt[39] had presses made of the type illustrated in figure 129, with cheeks of glazed procelain. The lower part is 250 mm. square, and is surrounded by a channel which collects the expressed liquid, and this if abundant, runs off through a spout. The upper portion is a pyramid 153 mm. square and 85 mm. thick, whose truncated top is held and surrounded by a cast iron crown lined with rubber. The pressing surfaces of both cheeks are well polished and have channels crossing each other and providing exits for the liquid pressed out. The 2 cheeks lie free in their frames so that they may be removed at any time and cleaned. The porcelain cheeks withstand the considerable pressures exerted by the screw press without being crushed. Hydraulic presses are used for stronger pressing. A press of this kind capable of exerting 500 atmospheres pressure is in use in the Berlin laboratory.

[39] Witt, Otto N., *Ber.*, 26, 1695 (1893).

CHAPTER XII

CRYSTALLIZATION

CRYSTALLIZATION FROM HOT OR EVAPORATING LIQUIDS

Organic compounds are brought into crystalline form by dissolving them in suitable solvents. In most cases, these are saturated with the material to be recrystallized after they have been heated to boiling. The substance separates in crystalline form when the solution cools. The liquid must be allowed to cool slowly if large crystals are desired. For example, the filtrate of hot saturated solution which has already begun to crystallize in the beaker during the filtration, is reheated to redissolve the crystals. The beaker is then placed in the water of a water bath heated to the proper temperature, that is, to boiling for aqueous solutions, to 80° for alcoholic solutions and so on, and the whole covered with a cloth. If this is done, for instance, when recrystallizing 5 grams of crude hippuric acid from boiling water, crystals 5 to 6 cm. long, may be obtained. Meyer[1] has described a method of obtaining uniform, single crystals of very remarkable size. Exposure to air is said to play an essential part with respect to supersaturated solutions, in that it causes[2] the separation of crystals from solutions only very slightly supersaturated. According to this patent, highly supersaturated solutions can only be obtained in the absence of air, and these, later, will deposit very large crystals.

Easily volatile solvents, such as ether, chloroform, carbon bisulfide are frequently used for recrystallization. The crystals separate as the solvents gradually disappear. To obtain more crystals from hot solutions than separate by cooling to room temperature, it is often well to strongly cool the solutions themselves, or the mother liquors after removing the first crop of crystals. This procedure has been well developed technically. In the laboratory, water should not be chosen for this purpose, since the solvent should not solidify, but rather carbon bisulfide, freezing at[3] −116°; 95 per cent alcohol (−130°);[4] ether (−117°); toluene (−97°); chloroform (−63°).[5]

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[1] Meyer, F., *Archiv. Pharm.*, [3], **13** (1878).

[2] Bock, I., French patent 369729 (1906); *Ch. Zt. Rep.*, **31**, 84 (1907).

Cabot[6] states the following regarding petroleum ether: 10 cc. of gasoline (d. 0.698), in a test tube, was placed in the neck of a silvered double walled flask containing liquid air and was cooled, while being stirred with a pentane thermometer. At −110° the gasoline was still liquid, at −125° it had the consistency of vaseline and rapidly became harder as the temperature fell. Another sample (d. 0.713) began to thicken at −120°, and was as hard as horn at −147°. No evidence of crystallization was observed.

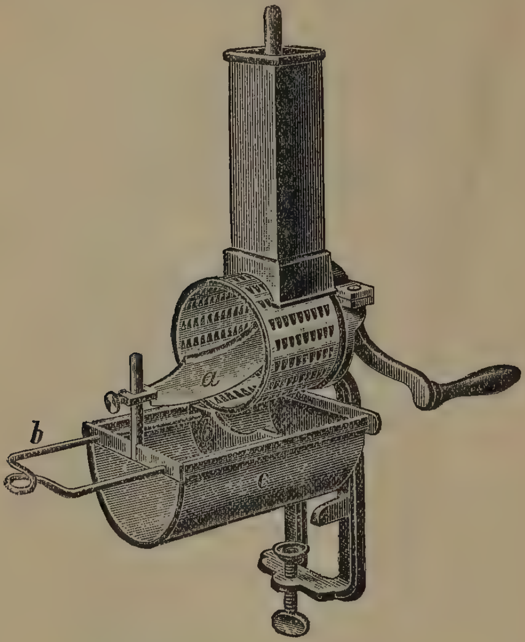

Fig. 130. Ice Grinding Mill (Schwalbe)

Freezing mixtures, which will be discussed separately, are only efficient if the warmer layers formed are continually destroyed by constant stirring. A mixture of about equal parts of salt and snow (described as early as 1626) producing −17°, or a mixture of calcium chloride and snow, producing −48°, may be used. Snow is prescribed as one of the constituents but it is seldom available, and finely pounded ice must usually be substituted for it. This is not as efficient as the fine snow, and furthermore it is not easy to break up ice uniformly by the usual method of wrapping large pieces in a cloth, and pounding with a hammer. This fact led Schwalbe[7] to design an ice mill. In this (fig. 130), the ice in coarse chunks is fed into the hopper from above and pressed against a revolving sieve with moderate pressure by means of a block of wood provided with a handle. The edges of the holes of the sieve are turned up and shave the ice off the larger pieces; the ice meal falls through the holes of the sieve, part of them directly into a receptacle *c*, and part of them into the inside of the drum. The scraper *a*, a piece of sheet iron, set at an angle to the axis of the drum, forces the ice meal out of the holes. The powdered ice can be easily removed from the receptacle *e*, by pulling out the scraper *b*, and caught in a piece of sheet iron. The mill works at its best only after its walls have been cooled to the melting point of ice. Since they are made of thin sheet iron, they cool quickly. The product is practically dry ice meal, and the capacity is about 1 kilo in five to seven minutes. The mill can readily be taken apart and the pieces easily dried and so kept from rusting.

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[3] Wroblewski, S., and Olzewski, K., *Monatsh.*, **4**, 338 (1884).

[4] Ladenberg, A., and Krügel, C., *Ber.*, **33**, 638 (1900).

[5] Archibald, E., and McIntosh, D., *J. A. C. S.*, **26**, 305 (1904).

[6] Cabot, G., *J. S. C. I.*, **26**, 813 (1907).

If the temperatures attained with snow or ice are not low enough, solid carbon dioxide is made into a mush with ether and the vessel placed in it. This mixture, if well stirred gives a temperature of −80°, and by using a vacuum, it is possible to reach −103° with it. According to Ruff, a liquid having the temperature of −60 to −80° is easily obtained by adding some liquid air to absolute alcohol. Hempel[8] has given extensive directions for working at very low temperatures. Reference only is made to this since it is not often done.

A very rare case, whose discovery is practically always due to accident, occurs when any indifferent organic material which can be made to crystallize with extreme difficulty, forms a well crystallized, double compound with an inorganic salt. Grape sugar is an example of this, and in 1825, Calloud,[9] while investigating the urine of diabetics, found that this sugar combines with sodium chloride, and forms crystals, a centimeter in size, of the formula, $2C_6H_{12}O_6 \cdot 2NaCl \cdot H_2O$. These are obtained in the anhydrous form when they are precipitated from their concentrated solution by methyl alcohol.[10] Until Fischer, in 1885 discovered the osazone, this was the only way of obtaining solid grape sugar from diabetic urine.

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[7] Schwalbe, C., German patent 167965; *Chem. Zentr.*, **73**, I, 509 (1902).

[8] Hempel, Walther, *Ber.*, **31**, 2993 (1898).

Bergell[11] found that 1 molecule of hexamethylene-tetramine combines with 2 molecules of sodium acetate and 6 of water to form a stable double salt which is produced by bringing these constituents together, and evaporating.

Mikolajczak, the discoverer of mononitro-glycerol, observed the separation of small quantities of crystals when treating a diluted mixture of glycerol and nitric acid with calcium carbonate. These were found to be a compound of glycerol mononitrate with calciumnitrate, $Ca(NO_3)_2 \cdot 3C_3H_5(OH)_2(NO_3) \cdot H_2O$, and when decomposed with potassium sulfate, produced pure glycerol mononitrate.[12] The anhydrous salt is obtained by recrystallization from alcohol.

Crystals are also obtained by sublimation. Other methods of producing them are practically never applied to organic materials.

The ingenious procedure used in 1905 by Urbain and Lacombe in separating the terbium earths, which up to that time had been so difficult to handle, may perhaps, be applied to two organic compounds very similar to each other, and very difficult to separate by recrystallization. Bodman had observed that bismuth nitrate crystallizes isomorphically with the nitrates of the rare earths. Accordingly, they added a certain quantity of magnesium-bismuth nitrate to the magnesium double nitrates of their rare earths. When fractionally crystallized, the magnesium-bismuth nitrate appears between the double nitrate of samarium and europium, so that their separation, which otherwise is extraordinarily difficult, is now accomplished quantitatively, with comparative ease. The preparation of pure europium and terbium by a similar method by which they obtained the rarest of the "rare earths" is a triumph of skilful application of an extremely refined method.[13] This principle of separating two closely related bodies that cannot be completely separated by fractional crystallization, by introducing a third material is surely very ingenious and perhaps applicable to organic chemical problems.

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[9] Calloud, *J. Pharm.*, [2], **11**, 564 (1825); see also Lippmann, E., *Chemie der Zuckerarten*, Braunschweig, 1904, p. 549.

[10] Fischer, E., and Schidmer, E., *Ann.*, **272**, 165 (1893).

[11] Bergell, P., and Wülfing, A., United States patent 852993; *Chem. Abstr* . **1**, 2188 (1907).

[12] Mikolajczak, A., Will, W., *Ber.*, **41**, 1118 (1908).

CRYSTALLIZING MEDIA

The following solvents, or suitable mixtures of them, are used for dissolving materials to be crystallized. It is most essential that they have no chemical action on the material to be recrystallized. The inorganic media to be considered are water, hydrochloric acid, sulfuric acid, and the organic media are acetone, ether, ethyl alcohol, formic acid, amyl alcohol, benzene, chloroform, ethyl acetate, acetic acid, methyl alcohol, nitrobenzene, petroleum ether, phenol, pyridine, carbon bisulfide, toluene.[14]

The solvents named below are not used so frequently. In certain cases, one of these is the only solvent which will give the desired result and its use, which at first glance, may seem somewhat forced, so that its inclusion in this list seems superfluous, is really a necessity. It should be pointed out that the esters of organic (also inorganic) acids are widely used as solvents in technical practice and it may be that they are much more suited to laboratory purposes, than is usually assumed.

Ethyl benzoate,[15] allyl alcohol,[16] formic acid,[17] methyl formate,[18] amylal,[19] aniline,[20] azobenzene,[21] quinaldine,[22] quinoline,[23] cumene,[24] cyclohexanol, cyclohexyl formate,[25] dimethyl aniline,[26] epichlorhydrin,[27] hydrofluoric acid,[28] glycerine,[29] hexane,[30] isobutyl alcohol,[31] Canada balsam[32] or colophony,[33] cresol, methyl ethyl ketone,[34] ethyl lactate,[35] naphthalene, oleic acid,[36] olive oil,[37] paraffin,[38] petroleum,[39] phthalic ester,[40] nitric acid, sulfurous acid,[41] tar oil,[42] turpentine,[43] thiophene,[44] xylene,[45] spermaceti.[46]

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[13] Urbain, G., and Lacombe, H., *C. r.*, **138**, 84 (1904).

[14] Carbon tetrachloride, iso-propyl alcohol, n-butyl alcohol, ethylene chlorohydrin, and ethylene chloride are now readily available and valuable solvents.—H. T. C.

[15] Gabriel, S., and Leupold, Ernst, *Ber.*, **31**, 1278 (1898).

[16] Mylius, F., *Ber.*, **19**, 373 (1886).

[17] Aschan, O., *Ann.*, **271**, 266 (1892).

[18] Bonwitt, G., *Ch. Zt.*, **44**, 974 (1920).

[19] Knoevenagel, E., and Weissgerber, R., *Ber.*, **26**, 439 (1893).

[20] Aguiar, A., and Bayer, Alex., *Ann.*, **157**, 367 (1871).

[21] Seidel, Paul, *Ber.*, **23**, 184 (1890).

[22] Bayer & Co., German patent 83046 (1892); Fr. III, 1011.

[23] Scholl, R., and Berblinger, H., *Ber.*, **36**, 3429 (1903).

[24] Dziewonski, K., *Ber.*, **53**, 2181 (1920).

CHOICE OF CRYSTALLIZING MEDIA

Although, in general, any solvent may be used as a crystallizing medium for any material soluble in it, nevertheless, the choice of the most suitable one is always worthy of consideration. (See therefore the heading "Solvents and Diluents.") Particularly, as is usually the case, when materials are to be purified in this way, one crystallizing medium may give results more rapidly than another, or it may be that there is only one that will serve the purpose. There are cases of bodies crystallizing from only certain solvents, while they separate amorphously or even as gels from others.

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[25] B. A. S. F., German patent 251351 (1911); *Chem. Zentr.*, **83**, II, 1246 (1912).

[26] Möhlau, R., and Fritzsche, E., *Ber.*, **26**, 1035 (1893); *Ch. Fabrik*, E. Schering, German patent 73354 (1893); Fr. III, 954.

[27] Flemming, H., *Ch. Zt.*, **21**, 97 (1897).

[28] Lenz, W., *Ber.*, **12**, 581 (1879).

[29] A. Leonhardt & Co., German patent 46252 (1888); Fr. II, 373.

[30] Willstätter, R., and Moore, C. W., *Ber.*, **40**, 2666 (1907).

[31] Latschinoff, P., *Ber.*, **20**, 3275 (1887).

[32] Gattermann, L., and Ritschke, A., *Ber.*, **23**, 1747 (1890).

[33] For study of crystallization under the microscope.

[34] Diels, O., and Abderhalden, E., *Ber.*, **36**, 3179 (1903).

[35] Bonwitt, G., *Ch. Zt.*, **44**, 974 (1920).

[36] Remy & Erhart, German patent 38417 (1886); Fr. I, 304.

[37] Also used frequently as harmless solvent for substances that are to be injected subcutaneously into animals.

[38] B. A. S. F., German patent 61711 (1890); *Ber.*, **25**, R, 488 (1892).

[39] Täuber, E., and Loewenberg, R., *Ber.*, **24**, 2597 (1891).

[40] Hesse, A., German patent 251237 (1911); *Chem. Zentr.*, **83**, II, 1246 (1912).

[41] Bayer & Co., German patent 68474 (1892); Fr. III, 194.

[42] Perkin, A. G., *Ber.*, **24**, R, 652 (1891).

[43] Zwenger, C., *Ann.*, **66**, 7 (1848).

[44] Liebermann, C., *Ber.*, **26**, 853 (1893).

[45] Farbwerke Meister Lucius und Brüning, *Ber.*, **25**, R, 185 (1892); German patent 57944 (1890); Fr. III, 23.

[46] Wartha, V., *Ber.*, **4**, 334 (1871).

In this connection, methyl alcohol may behave so differently from ethyl alcohol that the former may be used when the other simply cannot be. This is shown by the following observations. As early as 1840, Wiggers[47] described a plant base derived from the American velvet leaf, which he could not crystallize. It came into commerce for a long time as a brown powder, under the name Bebeerinum purum. According to Scholtz,[48] this consists of crystallized Bebeerinum together with considerable oxidation product. By means of ether, he was able to remove the base from the extract in a comparatively pure state, but it could only be recovered as a yellow powder. It dissolves easily in ethyl alcohol and separates amorphously from it also. It exhibits the same behavior with chloroform and acetone. In 1898, further experiments showed that it dissolves just as easily in methyl alcohol as in ethyl alcohol, even in the cold, but while it separates amorphously from the latter, but not until the solution is evaporated, after about a minute the methyl alcohol solution begins to deposit crystals so rapidly that the liquid is converted to a crystalline magma in a short time. These crystals do not contain any methyl alcohol of crystallization.

The observations of Pawlewski[49] will serve as an example of the separation of crystallizable bodies in the gel form. A 1 per cent solution of paraffin in benzene obtained at 20°, if cooled about 5 to 7°, solidifies to a uniform gel which cannot be poured from the container. When a 2.2 per cent solution in benzene is cooled, so thick a gel is formed that it can support a load of several grams withouts losing its coherence. Solutions in *p*-xylene behave similarly. The solution of 3.53 grams paraffin in 100 grams chloroform, at 25 to 27°, forms so consistent a gel when cooled to 18° that it will support 300 grams without being crushed. The paraffin which separates is greatly swollen, like boiled starch. Solutions of paraffin in carbon bisulfide and in turpentine act similarly. However, the most characteristic action of paraffin is toward ether. Thin shavings of paraffin, cut with a razor, fall to a fine powder when covered and mixed with ether, a part of the paraffin dissolving. After the solu-

[47] Wiggers, A., *Ann.*, **33**, 81 (1840).

[48] Scholtz, M., *Ber.*, **29**, 2054 (1896).

[49] Pawlewski, Br., *Ber.*, **23**, 327 (1890).

tion stands for twelve to twenty hours and is then cooled only 2°, the paraffin separates in the form of greatly swollen flocks very similar to mucilage or a gel. When the paraffin separates from these solutions, not a trace of crystallization can be observed by the naked eye or under a microscope. The behavior of paraffin toward acetic acid is different. When these solutions, whether saturated or unsaturated, are cooled, the paraffin always precipitates as small scales or leaflets which separate completely from the solvent. In this case Pawlewski was not able to obtain a gel by any method. Even boiling acetic acid solutions deposited the paraffin in scales when cooled. Paterno[50] observed a similar behavior of other materials toward various solvents.

DETAILS CONCERNING INDIVIDUAL CRYSTALLIZING MEDIA

Under this heading will be found statements concerning the individual crystallizing media, while the next division will treat of the recovery of crystals from solutions and mother liquors, as well as recrystallization.

WATER, HYDROCHLORIC ACID, SULFURIC ACID

If materials are to be recrystallized from water and are acted upon by the oxygen of the air and, for instance, are colored by it as are many amines, some hydrogen sulfide is added to the water. Water of crystallization is found in the most varied proportions, from one-sixth of a molecule of certain carbohydrates, to two-thirds of a molecule with phenyldihydro-β-naphthotriazine,[51] etc. Such water of crystallization is sometimes retained with extraordinary tenacity. Thus the barium salt of an acridone-sulfonic acid does not lose its 1.5 molecules of water until heated to 220°.[52]

The behavior of citric acid[53] with respect to water of crystallization is very remarkable. According to Witter, if its solution is evaporated until the temperature has risen to 130°, anhydrous acid crystallizes, on cooling, and this, when recrystallized even from cold water, separates again in the anhydrous form. If, however, a crystal of the ordinary hydrated crystallized citric acid is put into the solution, a hydrated product results. This strange characteristic is retained by even the lead salts, as shown by the behavior of the acids recovered from them.

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[50] Paterno, E., *Gaz. chim. ital.*, **19**, 1 (1889).

[51] Goldschmidt, Heinrich, and Poltzer, August, *Ber.*, **24**, 1003 (1891).

[52] Schöpff, M., *Ber.*, **25**, 1981 (1892).

[53] Witter, H., *Ber.*, **25**, 1159 (1892).

Hot hydrochloric acid is very useful because it does not dissolve many gummy substances while dissolving the crystallizable principal material. Thus, crude *p*-nitrophenol is crystallized from it, and all the tars adhering to it (from its preparation) remain undissolved; the same is true of bromonitrophenol[54] and of py-1,3-dihydroxyquinoline,[55] etc.

Concentrated sulfuric acid may be of assistance when all other crystallizing media have failed. For example, with its aid, Baeyer[56] was able to obtain crystalline bichlorhydurilic acid by dissolving it in the concentrated acid, and then re-precipitating it by carefully adding water. Many sulfonic acids which separate from water only in the form of gums, crystallize easily from dilute sulfuric acid, as was observed for instance, by Lönnies,[57] in the case of γ-sulfo-isophthalic acid.

Baeyer[58] prepared triphenyl carbinol sulfate, pure enough for analysis, in the following very remarkable way. The crystals obtained by adding concentrated sulfuric acid to the chloroform solution of trichlortriphenyl carbinol are exceedingly sensitive to the moisture of the air, and consequently could not be freed of the adhering sulfuric acid which was more or less diluted with water, by spreading on clay plates. The uncombined sulfuric acid is best removed by using chloral, which in the presence of an excess of the carbinol takes up the water present, forming chloral hydrate, and this, when once formed, does not again give up its water to the sulfate. Since chloral, furthermore, dissolves the sulfate, this offers the advantage that the sulfate may be formed in the presence of an excess of carbinol. The sulfate was prepared as follows: 2 grams trichlortriphenyl carbinol was dissolved in a little chloral and added to a mixture of 6 drops of concentrated sulfuric acid and a little chloral. This quantity of sulfuric acid is approximately equivalent to 0.75 gram of carbinol calculated from the determined composition of the sulfate. Consequently, about three times the requisite quantity of carbinol is contained in the chloral solution. The sulfuric acid dissolves completely on shaking; and the addition of an equal volume of chloroform to the deep orange liquid, causes, after some time, the separation of the sulfate in the form of brown prisms. The material was prepared for analysis by washing the crystals with chloroform and then drying to constant weight in a vacuum desiccator over soda lime. Any admixed chloral hydrate volatilized easily. Since water wets the sulfate poorly, the latter was covered with alcohol, water added, and then filtered. The sulfuric acid in the filtrate was precipitated by barium chloride.

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[54] Schlieper, F. W., *Ber.*, **25**, 552 (1892).
[55] Baeyer, A., *Ber.*, **15**, 2151 (1882).
[56] Baeyer, A., *Ann.*, **127**, 26 (1863).
[57] Lönnies, Hermann, *Ber.*, **13**, 704 (1880).
[58] Baeyer, Adolf, *Ber.*, **38**, 1161 (1905).

ACETONE, ETHER, ETHYL BENZOATE, FORMIC ACID

Acetone is just as useful a crystallizing medium as is ether which is so frequently employed. According to Arnoult,[59] pure acetone is obtained by adding 4 grams potassium permanganate and 6 grams crystallized soda, both dissolved in 100 cc. of water, to 1 liter of commercial acetone. This is allowed to settle and the acetone distilled. However, materials dissolved in acetone, may be caused to separate by the addition of water, or acetone may be mixed with water and its solvent power with regard to the material to be recrystallized easily modified. It is even better than ether in this respect. Especially pure acetone is obtained by distilling it several times over potassium permanganate[60] and then drying it with potassium carbonate. Cholalic acid[61] combines with 1 molecule; camphoric acid[62] with 0.5 molecule of it, as acetone of crystallization.

Commercial ether usually reacts acid.[63] It is purified by shaking it with sodium hydroxide solution. The ether separated from the latter is then shaken again with water. If, after some time, it is again tested, traces of acid will again be found. The preparation of absolute ether will be discussed under the heading "Drying of Solids, etc."

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[59] Arnoult et Jumeau, Seine, French patent 386181; *Chem. Abs.*, **3**, 2351 (1909).

[60] Sachs, F., *Ber.*, **34**, 501 (1901).

[61] Mylius, F., *Ber.*, **19**, 373 (1886); *Ber.*, **20**, 1975 (1887); Latschinoff, P., *Ber.*, **20**, 3275 (1887).

[62] Pope, W. J., *J. Chem. Soc.*, **69**, 1696 (1896).

[63] Mylius, F., and Foerster, F., *Ber.*, **24**, 1491 (1891).

It is difficult to obtain commercial ether entirely free of alcohol.[64] Cowie[65] investigated different varieties of commercial ether. The best test for alcohol is aniline violet, for aldehyde potassium hydroxide. None of the samples gave a reaction with bichromate. Water is most certainly detected by carbon bisulfide. Kempf[66] states that the ordinary laboratory ether, after standing sometime in the light, develops such energetic oxidation action that it quickly decolorizes indigo solution in extraction apparatus. This process appears to proceed more rapidly in the light than in the dark. (See also the discussion of ether under the heading "Shaking Out.") Alcohol may be removed from ether by boiling with sodium, under a reflux, and then distilling; the sodium alcoholate remaining behind.

Ether solutions from which crystals for crystallographic measurements are to be prepared, are best dried with calcium chloride before allowing them to evaporate, if anhydrous ether was not used at the start. Otherwise, there will remain on the crystals, the water which was dissolved in the ether, even though the last of the ether adhering to the crystals is evaporated in the desiccator. This dulls their reflecting surfaces and unfits them for measurements.

Ether causes many materials to crystallize from water, if their solutions are covered with it. Thus glycocholic acid is obtained from ox-gall from the neighborhood of Tübingen[67] (the other regions furnished material too poor in this,[68] a very unusual occurrence in which the food exhibits so much physiological significance). The ox-gall is placed in a cylinder and covered with some ether and 1 cc. pure concentrated hydrochloric acid is added to each 20 cc. The crystalline acid easily separates after several days. Its preparation from galls derived from other regions is, on the contrary, a very tedious procedure.[69]

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[64] J. F. Norris has pointed out that commercial ethyl ether may be almost completely freed of alcohol and water by shaking it with 50 per cent sulfuric acid. Subsequent distillation is of course advisable. Ether which has been allowed to stand for some time in partially filled containers is liable to contain peroxide.—H. T. C.

[65] Cowie, W. B., and Broadbent, T. O., *Pharm. Jour.*, **81**, 366 (1908).

[66] Kempf, Richard, *Ch. Zt.*, **34**, 1366 (1910).

[67] Hüfner, G., *J. pr. Ch.*, [2], **25**, 97 (1882).

[68] Emich, F., *Monatsh.*, **3**, 335 (1882).

[69] Strecker, A., *Ann.*, **65**, 7 (1848).

Wallach[70] found that the heavy metal salts of fenchocarboxylic acid, which are difficultly soluble in water, are partially soluble in solvents such as ether, chloroform, benzene, which ordinarily do not dissolve such salts.

Ether occasionally combines as ether of crystallization. Thus Fischer and Ziegler[71] obtained crystals of pseudo leucaniline containing ether of crystallization, and Fischer and Hepp[72] found that when Magdala red was recrystallized from absolute ether it formed crystals, which after drying in a vacuum, gave analytical results corresponding to the formula $C_{30}H_{20}N_4 + 1.5(C_2H_5)_2O$. This ether is evolved when the crystals are heated in a xylene bath, and the residue corresponds to the formula $C_{30}H_{20}N_4$. Tellurium and titanium tetrachloride[73] also separate with 1 molecule of ether of crystallization. This fact may perhaps be used in preparing absolutely pure ether.

Reference should again be made to the fact that explosions sometimes occur when ether is distilled. (For details see the heading "Extraction.")

Although ether is generally used as a crystallizing medium and as a diluent, purposes for which it is well suited because of its indifference, there are cases in which it takes part in reactions. Under such conditions, it should not be used. It behaves thus in the presence of aluminium chloride, for Jannasch[74] states that the best method of preparing hexaethyl benzene is the treatment of a mixture of benzene and ether with aluminium chloride. He ethylated phenols in the same way.[75] Wedekind[76] found that 50 per cent of the theory of ethyl benzoate is obtained by mixing benzoyl chloride with ether and adding anhydrous sublimed ferric chloride. Likewise, Descudé[77] found that although ether and acetyl chloride do not react with each other, ethyl acetate is formed when zinc chloride is added:

$$CH_3{-}COCl + C_2H_5\,OC_2H_5 = CH_3{\cdot}COO{\cdot}C_2H_5 + C_2H_5Cl$$

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[70] Wallach, O., *Ann.*, **300**, 300 (1898).

[71] Fischer, Otto, and Ziegler, Joseph, *Ber.*, **13**, 673 (1880).

[72] Fischer, O., and Hepp, E., *Ann.*, **286**, 235 (1895).

[73] Rust, E., *Ber.*, **30**, 2828 (1897).

[74] Jannasch, P., and Bartels, A., *Ber.*, **31**, 1716 (1898).

[75] Jannasch, P., and Rathjen, A., *Ber.*, **32**, 2391 (1899).

[76] Wedekind, E., and Haeussermann, J., *Ber.*, **34**, 2081 (1901).

[77] Descudé, M., *C. r.*, **132**, 1129 (1901).

In this instance, these three reagents do not cause the elimination of hydrochloric acid as they usually do, but rather of ethyl chloride.

In many cases, ethyl benzoate is a very useful crystallizing medium. Thus Will[78] used it for recrystallizing his δ-tetranitro-naphthalene which is hardly soluble in other organic solvents, and with the exception of this solvent it can only be recrystallized from very concentrated nitric acid. Gabriel[79] recrystallized nitronaphthacene quinone from it.

Sometimes it does not act as a crystallizing medium but instead, benzoylates the compound to be purified. Thus Kehrmann and Bürgin[80] found that it was a general characteristic of the monoalkyl-fluorindines to be converted more or less rapidly into the benzoyl derivatives when boiled with ethyl benzoate, while diphenyl-fluorindine could be recrystallized unchanged from this solvent. (This reaction is analogous to the conversion of ethyl benzoate into benzamide by ammonia, and in this case, may be explained by the rather strongly basic nature of the monoalkyl-fluorindines.)

Artificial musk, which is difficulty soluble in practically all the customary solvents, dissolves up to 20 per cent in benzyl benzoate.[81]

Aschan[82] found that 95 per cent formic acid is the only crystallizing medium for α-brom-hexahydro-benzoic acid, and since then he has used it with great success for mono- and dibrom-carboxylic acids. In many instances, it is a better solvent than glacial acetic acid, and excels it in the much greater difference of the solubility at the boiling point and when cold. A further advantage is its greater volatility on the water bath. One disadvantage is the fact that it is easily oxidized by inorganic reagents such as chloric acid, chromic acid etc. It also esterifies alcohols, borneol, for instance, even at room temperature.

ALCOHOLS

Methyl, ethyl, amyl alcohol, etc.

Next to water, ethyl alcohol is most frequently used as a crystallizing medium. Its availability and low price have contributed to this. Ordinary ethyl alcohol always contains acetaldehyde. For this reason, it cannot be used for making stable alcoholic potash or sodium hydroxide solutions and as is well known, they always turn brown quickly. Dubovitz[83] has described the most convenient method of freeing ethyl alcohol from aldehyde. For this purpose, 5 cc. of 50 per cent sodium hydroxide and 5 grams of zinc dust are added to each liter of alcohol and boiled one-half hour under a reflux. The aldehyde is reduced to alcohol, and consequently the distillate remains clear and colorless, even after hours of boiling with concentrated lye. For the preparation of absolute alcohol, see the heading "Drying of Solids, etc."

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[78] Will, W., *Ber.*, **28**, 369 (1895).

[79] Gabriel, S., and Leupold, Ernst, *Ber.*, **31**, 1278 (1898).

[80] Kehrmann, F., and Bürgin, H., *Ber.*, **29**, 1248 (1896).

[81] Koehler, *Pharm. Zt.*, **49**, 1083 (1904); Mann, H., *Seifensiederzeit*, **32**, 234 (1905).

[82] Aschan, O., *Ann.*, **271**, 266 (1892); *Ch. Zt.*, **37**, 1117 (1913).

In general, methyl alcohol is intermediate between water and ethyl alcohol, consequently, for many purposes, it is much more useful than ethyl alcohol. Lobry de Bruyn[84] has discussed this in detail and it will be useful in many cases to know the most important points. This solvent, as well as the many differences in behavior between methyl and ethyl alcohol, has been discussed under the heading "Solvents and Diluents," and this may be kept in mind when choosing a crystallizing medium.

Working with ethyl alcohol is, in general, exactly like using water or any other solvent. It may be used mixed with water, or the substance may be dissolved in 96 per cent alcohol, filtered if necessary, and then almost boiling water added to the filtrate until a turbidity appears. It is then allowed to cool in the water bath in which the alcoholic solution was heated. It is always advisable to heat alcoholic solutions in a water bath rather than over a free flame. It takes considerably longer to bring the alcohol to a boil on the water bath, but over the free flame there is danger of fire with consequent loss of the substance.[85]

Certain compounds are soluble to about the same extent in hot or even dilute, cold alcohol, but insoluble in water. Therefore, they may often be crystallized by evaporating, on the water bath, the alcoholic solution to which much water has been added until it begins to cloud because of lack of alcohol, and on cooling, crystals will then be obtained. Sometimes only alcohol of a very definite strength can be used. Thus, according to Kiliani,[86] digitonin is easily crystallized from 87 per cent alcohol, while it separates only amorphously from stronger alcohol, and the precipitation is less complete and usually just as amorphous, from weaker alcohol.

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[83] Dubovitz, H., *Ch. Zt.*, **46**, 654 (1922).

[84] Lobry de Bruyn, C. A., *Z. ph. Ch.*, **10**, 782 (1892); *Ber.*, **26**, 268 (1893).

[85] Distillation of ethyl alcohol and even methyl alcohol, may be advantageously carried out under slightly reduced pressure, if the receiver is cooled in running water.—H. T. C.

It seems, according to Herzfeld,[87] that still more care must be taken when crystallizing maltose. It proceeds much more easily if the solution in hot 80 to 85 per cent alcohol, is allowed to stand in a closed vessel in a cold place, and only then should the alcohol be allowed to evaporate. It may be that during the heating, the maltose is converted to a deliquescent hydrate which is not retransformed to the anhydride until it has stood in the cold for some time.

The barium salt of choleic acid has been found by Mylius[88] to have the remarkable property of being insoluble in absolute alcohol as well as in water, but readily soluble in dilute alcohol.

Some organic sodium salts can only be obtained in crystalline form by dissolving them in absolute alcohol, and precipitating the solutions with ether. In the course of a few days the precipitate becomes crystalline. In this way, as was discovered as early as 1844 by Platner,[89] it is possible to obtain the so-called crystallized gall, which is known to be a mixture of the sodium salts of taurocholic and glycocholic acids.

Many materials that are prone to separate amorphously may be obtained crystalline with the aid of a mixture of water, alcohol and ether. This method is less used than it deserves. For instance, Partheil[90] prepared the hydrobromide of cytosine by neutralizing the concentrated water solution of the base with 25 per cent hydrobromic acid. He obtained from this solution the compound in the form of crystals by adding absolute alcohol and then a layer of ether. According to Bayer,[91] if water is added to an alcoholic solution of cholalic acid until a permanent turbidity appears, and then some ether is poured on this, the acid will crystallize in clumps.

It sometimes happens that acidified alcohol is preferable to neutral alcohol. A few drops of glacial acetic acid, etc., are used for this purpose. Thus it was thought that caffein sulfate was difficult to prepare until Biedermann[92] found that the salt could be obtained with surprising ease if the alkaloid is dissolved in about ten times the quantity of hot alcohol made strongly acid with sulfuric acid, and the solution then allowed to stand in a cool place for some time.

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[86] Kiliani, H., *Ber.*, **24**, 339 (1891); *Arch. Pharm.*, **231**, 460 (1893).

[87] Herzfeld, A., *Ber.*, **12**, 2120 (1879).

[88] Mylius, F., *Ber.*, **20**, 1970 (1887).

[89] Platner, E., *Ann.*, **51**, 105 (1844).

[90] Partheil, A., *Ber.*, **24**, 636 (1891).

[91] Bayer, H., *Z. physiol. Ch.*, **3**, 303 (1879).

Ammoniacal alcohol is also used, and Hofmeister[93] believes it to be the best medium for recrystallizing many amino acids, such as leucine (aminoisocaproic acid), tyrosine (aminohydro-para-coumaric acid). However, ammonium salts may be easily formed with strong amino acids.

According to Nencki,[94] crystalline para-hemoglobin is only obtained by shaking it in a closed flask with absolute alcohol saturated with ammonia at 0°, and filtering the solution into a flat dish so that the alcohol and ammonia may volatilize rapidly. A part of the para-hemoglobin separates on the bottom as a heavy crystalline precipitate, while the rest is oxidized through contact with the air, to albumin and hematin.

Organic acids are occasionally partially esterified by simple boiling with alcohol. This is of little importance as a method of preparing esters, but the phenomenon is sometimes encountered when recrystallizing acids from alcohol. For instance, apparently large quantities of cholalic acid disappear in the mother liquors which are obtained in large quantities when this compound is recrystallized from alcohol. The writer[95] has shown that it goes over to the ethyl ester which will not crystallize out. To avoid this, when dealing with acids having such properties, acetone, benzene, etc., should be used for recrystallization. This esterification may give rise to large errors, particularly in ultimate analysis, if the ester later crystallizes out along with the acid. This, of necessity, must result in too high a carbon content, which in turn, leads to the calculation of false formulae for the acids analyzed. This happened, for instance, in the case of dehydrocholic acid.[96] The presence of any ester in the acid, after recrystallization from alcohol, may be detected by the fact that although the crystals should consist of a pure acid, they will no longer completely dissolve in sodium carbonate solution.

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[92] Biedermann, H., *Arch. Pharm.*, **221**, 181 (1883).

[93] Hofmeister, F., *Ann.*, **189**, 16 (1877).

[94] Nencki, M., *Arch. Path. u. Pharm.*, **20**, 332 (1886).

[95] Lassar-Cohn, *Z. physiol. Ch.*, **16**, 497 (1892); *Z. physiol. Ch.*, **22**, 196 (1896).

[96] Lassar-Cohn, *Ber.*, **25**, 805 (1892); *Ber.*, **14**, 72 (1881).

Graham was the first to note that crystals could include not only water of crystallization, but also alcohol of crystallization. It has been found in the course of time, that practically every crystallizing medium may enter into molecular combination with the crystals separating from it. Such instances were pointed out in connection with ether, and more will be encountered in the discussion of other crystallizing media. Although this is no longer considered remarkable, it seemed so to Graham's contemporaries, and at first their explanation of the phenomenon was partly wrong. Not only are crystals containing alcohol of crystallization, such as cholalic acid, $C_{24}H_{40}O_5+C_2H_6O$ known, but Hesse has found a compound, conchairamine,[97] an alkaloid closely related to quinine, which contains at the same time, one molecule of alcohol of crystallization and one of water of crystallization, $C_{22}H_{26}N_2O_4+H_2O+C_2H_5OH$. On the other hand, Liebermann and Cybulski[98] found that hygrinic acid, even though recrystallized from ether-alcohol, retains its molecule of water of crystallization, indeed it easily reabsorbs it from the air. According to Hesse,[99] the hydrobromide of hyoscine crystallizes anhydrous from absolute alcohol, with $\frac{1}{2}$ molecule H_2O from 97 per cent; with 1 molecule H_2O from 93 per cent and with 2 molecules H_2O from 60 to 80 per cent alcohol. It crystallizes from water with 3 molecules H_2O. According to Wyrouboff,[100] cinchonidine hydrobromide crystallized from absolute alcohol has the formula, $C_{19}H_{22}N_2O \cdot HBr+\frac{1}{3}\ H_2O+\frac{1}{4}\ C_2H_6O$. That is, these crystals, obtained from absolute alcohol, contain 4 molecules of water and 3 molecules ethyl alcohol to each 12 molecules of salt. But perhaps this may all be calculated as alcohol, since $\frac{1}{3}$ molecule of H_2O is equal to 6, or approximately equal to $\frac{1}{8}$ molecule C_2H_6O, (molecular weight 46).

Methyl alcohol can, of course, be used for recrystallizing many materials. Friedrichs[101] discusses its impurities. The use of methyl alcohol in the chemical industry, especially for the preparation of aniline dyes, and likewise that of formaldehyde, has increased greatly in the last decades, and the requirements for the purity of the methyl alcohol have become much more stringent. The acetone content should not exceed 0.1 per cent. (The preparation of such methyl alcohol from crude wood spirit requires a series of fractionations with efficient column apparatus, and the systematic addition of hydrated lime, caustic soda and sulfuric acid at the various stages of the process. The difficulty of purifying crude wood spirit is due to the large number of compounds present in it, but it may be accomplished by the use of the above chemicals combined with careful supervision of the fractionation.) The greatest difficulty always is the removal of the last traces of acetone. While it is comparatively easy to produce methyl alcohol containing 1 per cent of acetone, the reduction of this content to 0.1 per cent is rather laborious.[102]

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[97] Hesse, O., *Ann.*, **225**, 247 (1884).

[98] Liebermann, C., and Cybulski, G., *Ber.*, **28**, 581 (1895).

[99] Hesse, O., *J. pr. Ch.*, [2], **64**, 361 (1901).

[100] Wyrouboff, G., *Ann. ch. ph.*, [7], **1**, 45 (1894).

[101] Friedrichs, F., *Ch. Zt.*, **32**, 891 (1908).

If materials that react with ketones are to be recrystallized, and they are rather numerous, methyl alcohol free from acetone[103] must be used so that the recrystallized substance is not contaminated with a condensation product. Occasionally, as stated above, it is superior to ethyl alcohol. Erdmann[104] recrystallized nitro-kata-dichlornaphthalene from a mixture of methyl alcohol and glycerol after unsuccessfully attempting to separate it from its isomers by means of other solvents.

Methyl alcohol, like ethyl alcohol, enters into crystals, *e.g.*, Wyrouboff obtained crystals of cinchonidine hydrobromide containing one molecule of methyl alcohol, $C_{19}H_{22}N_2O \cdot HBr + CH_3OH$. The hydrochloride of narcein[105] likewise crystallizes with one molecule of methyl alcohol, $C_{23}H_{27}NO_8 \cdot HCl + CH_3OH$.

Allyl alcohol exhibits a corresponding behavior, and thus cholalic acid[106] crystallizes with one molecule of it, $C_{24}H_{40}O_5 + C_3H_5OH$.

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[102] The removal of acetone from methyl alcohol by means of sodium hypochlorite is described by Menzies (*J. Chem. Soc.*, **121**, 2787 (1922)).—H. T. C.

[103] Acetone is detected by greatly diluting the liquid with water and adding several drops of a freshly prepared solution of sodium nitroprusside. If acetone is present a red coloration appears which is intensified by the addition of glacial acetic acid.

[104] Erdmann, H., *Ann.*, **275**, 258 (1893).

[105] Freund, Martin, German patent 71797 (1893); Fr. III, 975.

[106] Mylius, F., *Ber.*, **19**, 373 (1886).

Amyl alcohol is an excellent solvent for compounds which otherwise can scarcely be obtained as crystals. Thus Niementowski[107] used it to dissolve *m*-methyl-*o*-uraminobenzoyl, which is difficultly soluble in all other solvents, and on cooling it separated in needles. Nencki[108] states that the hydrochloride of hemin which may be prepared from the red blood corpuscles, crystallizes with one molecule of amyl alcohol, $C_{32}H_{31}ClN_4FeO_3+C_5H_{11}OH$; while, according to Küster,[109] the crystals contain only half so much amyl alcohol.

ANILINE, ANISOLE

Aniline is more frequently used as a crystallizing medium than is usually assumed. Thus 1,4-diamino-anthraquinone easily dissolves in it, and separates from the solution in shining bronze-like crystals, containing aniline of crystallization.[110]

Phenylglucosazone may be purified, according to Hougounenq,[111] by crystallizing the compound washed with cold water, first from anisole and then from dilute alcohol. Gnehm and Kaufler[112] crystallized methylene violet from anisole and were able, with its aid, in contrast to other solvents, to avoid excessive volumes of liquid.

BENZENE, QUINOLINE, CHLOROFORM

As Liebermann[113] has shown, commercial benzene (b.p. 80 to 82°), contains about 0.15 per cent thiophene and 0.2 per cent carbon bisulfide, and in certain cases, these may produce considerable side reactions. It should be possible to remove the latter by distilling the benzene after it has been thoroughly shaken with saturated alcoholic potash, which converts the carbon bisulfide into the non-volatile potassium xanthate. However, according to Schwalbe,[114] this procedure is not quantitative,[115] and complete removal is only accomplished by passing moist ammonia gas into the benzene, and in this way, completely converting the carbon bisulfide into a compound soluble in water:

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[107] Niementowski, S., *J. pr. Ch.*, **148**, 22 (1889).

[108] Nencki, M., and Sieber, N., *Ber.*, **17**, 2270 (1884).

[109] Küster, W., *Ber.*, **27**, 573 (1894).

[110] Bayer & Co., German patent 135561 (1900); Fr. VI, 298.

[111] Hougounenq, L., *J. Pharm.* [6], **4**, 235 (1897).

[112] Gnehm, R., and Kaufler, F., *Ber.*, **37**, 3032 (1904).

[113] Liebermann, C., and Seyewetz, A., *Ber.*, **24**, 788 (1891); Weger, M., *Z. angew. Ch.*, **22**, 339 (1909).

[114] Schwalbe, C., *Farb. u. Textilind.*, **3**, 462 (1904).

[115] The carbon bisulfide may be completely removed by stirring with methyl-alcoholic sodium hydroxide.—H. T. C.

$$CS_2 + 4\ NH_3 = NH_4CNS + (NH_4)_2S$$

According to Haller and Michel,[116] benzene may be freed of thiophene by heating it with 0.5 to 1 per cent of aluminium chloride, then washing with soda and distilling.[117] Benzene purified in this way does not show the isatin reaction, and does not darken when heated with sulfuric acid.

Montagne[118] obtained an amorphous silver salt of dichlorbenzilic acid which could be crystallized out of benzene only. According to Farnsteiner,[119] dry barium oleate does not dissolve in warm benzene. It dissolves very difficultly when boiled, even after the addition of absolute alcohol. On the other hand, it dissolves very easily when heated with benzene containing 5 per cent or even somewhat less of 95 per cent alcohol, and on cooling, crystallizes from the solution. If dry barium oleate is heated with benzene, and some water added, solution also occurs easily with subsequent crystallization. Barium oleate shows a similar behavior toward chloroform and petroleum ether.

Benzene combines with certain compounds as benzene of crystallization, and may be very firmly combined in these. Thus, Truhlar[120] found that thio-*p*-tolylurea had not entirely lost its three molecules of benzene of crystallization after 4 hours' heating at 100 to 110°. Liebermann and Limpach[121] recrystallized ψ-tropine from benzene and attempted to approximately determine the content of benzene of crystallization by heating to 70°. The weight never became constant because of continuous volatilization of the ψ-tropine and they finally proved the absence of benzene of crystallization by determining the nitrogen in fresh crystals. Kishner[122] states that triphenylmethane combines with benzene in such a way that when the triphenylmethane crystallizes it completely removes the benzene from a warm solution containing only a little of it. He used this to remove the last portions of benzene from hexahydrobenzene. Among the aliphatic compounds, the anhydride of aconitic acid, for example, crystallizes with benzene of crystallization.[123]

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[116] Haller, A., and Michel, E., *Bull. soc. ch.* [3], **15**, 390 (1896).

[117] Thiophene may be completely removed by stirring with aqueous mercuric sulfate solution.—H. T. C.

[118] Montagne, P., *Rec. trav. ch.*, **21**, 22 (1902).

[119] Farnsteiner, K., *Z. f. Nahrungsmittelchemie*, **2**, 9 (1898).

[120] Truhlar, Jos., *Ber.*, **20**, 669 (1887).

[121] Liebermann, C., and Limpach, Ludw., *Ber.*, **25**, 927 (1892).

[122] Kishner, N., *Ber.*, **24** R, 559 (1891); *J, Russ.*, **1**, 20–26 (1891).

Some materials difficultly soluble in benzene are more soluble in toluene and still more so in xylene.

The great similarity between benzene and thiophene led Liebermann[124] to recrystallize triphenylmethane and similar bodies from the latter. The triphenylmethane crystals, $CH(C_6H_5)_3+C_4H_4S$, include one molecule of thiophene of crystallization. The crystals soon effloresce when exposed to the air.

The use of quinoline as a crystallizing medium is exemplified by the following; indanthrene[125] is almost insoluble in most of the commonly used organic media. It dissolves with difficulty, with a green blue color, in boiling aniline and in nitrobenzene (1 part in about 5000 of the latter), but is somewhat more soluble, about in the ratio of 1:500, in boiling quinoline and forms a blue solution. It crystallizes from this solution in lustrous, blue, coppery needles[126] whose appearance suggests pure indigo.

Commercial chloroform generally contains some alcohol. This is removed by shaking with water, or the chloroform is allowed to stand for some time with calcium chloride which combines with the alcohol and, at the same time, dries the chloroform.[127]

According to Gordin and Merrell,[128] strong organic bases, on long boiling, may attack chloroform, as does potassium hydroxide:

$$4\ KOH + CHCl_3 = 3\ KCl + 2\ H_2O + HCOOK$$

so that they are thus transformed to the hydrochlorides. They particularly studied this with acetone-berberine when they boiled it for twelve hours with a mixture of alcohol and chloroform. The equation:

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[123] v. Vietinghoff-Scheel, K., *Ch. Zt.*, **31**, 118 (1907).

[124] Liebermann, C., *Ber.*, **26**, 853 (1893).

[125] Badische, A. S. F., German patent 129845 (1901); Fr. VI, 412; Bohn, R., *Ber.*, **43**, 999 (1910).

[126] Scholl, R., and Berblinger, H., *Ber.*, **36**, 3429 (1903).

[127] This alcohol is intentionally added, as it retards the decomposition of the chloroform into carbonyl chloride. It may also readily be removed by shaking with concentrated sulfuric acid.—H. T. C.

[128] Gordin, H., and Merrell, C. G., *Arch. Pharm.*, **239**, 636 (1901).

$$4C_{20}H_{17}NO_4 \cdot C_3H_6O + CHCl_3 + 4\ H_2O = \\ 3\ C_{20}H_{17}NO_4 \cdot HCl + 2\ H_2O + C_{20}H_{17}NO_4 \cdot HCOOH + C_3H_6O$$

indicates the probable formation of 3 molecules of hydrochloride and 1 molecule of berberine formate, and the yield of the first was 86 per cent of the theory. It should be noted that free berberine absorbs carbon dioxide from the air. Perhaps other strong bases, such as piperidine, which also absorbs carbon dioxide, will show a similar behavior. Since phenylhydrazine belongs in this class, the subject will be discussed again under the heading "Solvents and Diluents."

Chloroform of crystallization is not uncommon. However, up to the present time, chloroform is the only liquid, which has been obtained chemically pure by carrying it through the state of solvent of crystallization.[129] This procedure may be carried out technically. In the method devised by Anschütz,[130] salicylide is crystallized in combination with the chloroform as $C_{32}H_{34}+2CHCl_3$. Since none of the impurities of the chloroform are carried with it into the crystals, which contain 33.24 per cent of chloroform, it will immediately be chemically pure when distilled from the crystals. This method may serve for the absolute purification of other compounds which can only be obtained as liquids, and perhaps the method has a great future. Even ordinary ether has never been obtained as pure as might be possible by this method. Such ether would be particularly valuable for the determination of its physical constants.

Other compounds containing chloroform of crystallization may be mentioned. The triazine of benzene,[131] $C_{27}H_{18}N_6$, crystallizes with 1 molecule, colchicine[132] with 2 molecules, and leuco-ditoluylenequinoxaline[133] with 1 molecule of chloroform, which is completely removed from the last compound only at 140°. Schmidt[134] found chloroform so firmly held in berberine chloroform, $C_{20}H_{17}NO_4 \cdot CHCl_3$, that he doubted whether this body was a molecular compound formed by the simple addition of components which were still present as such. He found later[135] that this compound when dissolved in hot chloroform, may take up another molecule of chloroform which functions as normal chloroform of crystallization, *i.e.*, $C_{20}H_{17}NO_4 \cdot CHCl_3 + CHCl_3$. It is remarkable that, contrary to practically all other experience, Oudemans[136] found that cinchonine was more soluble in a mixture of alcohol and chloroform than in either of them alone.

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[129] This has also been done in the cases of acetone and methyl ethyl ketone, which form loose addition products with sodium iodide (*J. Chem. Soc.*, **103**, 1255 (1913); **129**, 2784 (1926)).—H. T. C.

[130] Anschütz, R., *Ann.*, **273**, 77 (1893); A-G. f. Anilin-Fabrikation, German patent 70614 (1892); Fr. III, 825.

[131] Nietzki, R., and Kehrmann, F., *Ber.*, **20**, 325 (1887).

[132] Zeisel, S., *Monatsh.*, **7**, 571 (1886).

[133] Nietzki, R., and Benckiser, Th., *Ber.*, **19**, 776 (1886).

If the content of chloroform of crystallization cannot be determined by the loss of weight suffered by the crystals when heated to a sufficiently high temperature, because the substance itself is already decomposed and therefore a constant weight of residue cannot be obtained, Schmiedeberg's[137] method may be used. He arrived at satisfactory results by removing the chloroform of crystallization in colchicine crystals with a current of steam. The chloroform was driven from the tube containing the crystals into another tube containing hot lime free from chlorine, and the chlorine in the second tube was subsequently determined.

GLACIAL ACETIC ACID, EPICHLOROHYDRIN, METHYLETHYL KETONE

If materials have been recrystallized from glacial acetic acid, the solvent adhering to the crystals may be removed by heating them in a drying tube at 100° in a current of air, or by allowing them to stand in vacuo over soda lime.[138] It also suffices to allow the glacial acetic acid to evaporate next to potassium hydroxide[139] in a desiccator not evacuated. Acetic acid of crystallization was found in the case of choleic acid, $C_{24}H_{40}O_4 + C_2H_4O_2$, by Latschinoff.[140] Hemin crystals are also said to contain it.[141]

Pawlewski[142] recrystallized *p*-dinitro-diazoamino-benzene from epichlorhydrin in which it is very soluble. Bishop's method of separating the two stereo forms of dinitrostilbene was laborious and wasteful; but Thiele and Dimroth[143] found that crystallization from epichlorhydrin was well suited to this purpose. When warmed, epichlorhydrin easily dissolves the higher melting ("trans") dinitrostilbene which preponderates. This is only slightly soluble in the cold, and after one crystallization is pure, and melts at 191 to 192°. This melting point is not changed by recrystallization from other solvents.

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[134] Schmidt, E., *Arch. Pharm.*, [3], **25**, 147 (1887).

[135] Gaze, R., *Arch. Pharm.*, [3], **28**, 625 (1890).

[136] Oudemans, A. C., Jr., *Ann.*, **166**, 74 (1873).

[137] Schmiedeberg, Dissertation, Dorpat, 1866, p. 19.

[138] Anschütz, R., and Kekule, Aug., *Ann.*, **228**, 303 (1885).

[139] Erlenmeyer, E., *Ber.*, **14**, 1867 (1881).

[140] Latschinoff, P., *Ber.*, **20**, 1046 (1887).

[141] Nencki, M., *Arch. Path. u. Pharm.*, **20**, 322 (1886).

[142] Pawlewski, Br., *Ber.*, **27**, 1566 (1894).

Diels and Abderhalden[144] oxidized cholesterol with alkaline bromine solution and obtained an acid $C_{20}H_{32}O_3$, which could not be easily crystallized. It was finally obtained pure by recrystallization from methyl ethyl ketone.

NAPHTHALENE, NITROBENZENE, PETROLEUM ETHER, PHENOL

Witt used naphthalene for recrystallizing α, β-naphthazine which could not be obtained crystalline in any other way. He dissolved it in the boiling hydrocarbon and extracted with hot alcohol the cake obtained on cooling. The crystalline azine remained behind. It is claimed in a patent[145] that nitro-alizarin blue, which is very difficultly soluble in the ordinary solvents, may be recrystallized from naphthalene.

Gabriel[146] used nitrobenzene for crystallizing nitro-ethine-diphthalide which separates from it in compact needles. Gräbe and Phillips[147] used it alone, or mixed with glacial acetic acid, to recrystallize a part of the dye obtained by the progressive hydroxylation of alizarin when this was heated with sulfuric acid.

The best petroleum ether consists of those fractions of the commercial product that distil from a water bath at 60 to 70°.[148] Wislicenus[149] calls the part of the petroleum ether, that after repeated rectification passes over completely between 33 and 39°, petrol pentane, while that boiling between 60° and 69°, he names petrol hexane.

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[143] Thiele, Johannes, and Dimroth, Otto, *Ber.*, **28**, 1412 (1895).

[144] Diels, Otto, and Abderhalden, Emil, *Ber.*, **36**, 3179 (1903).

[145] Meister Lucius & Brüning, German patent 59190 (1891); Fr. III, 249.

[146] Gabriel, S., *Ber.*, **19**, 837 (1886).

[147] Gräbe, C., and Philips, A., *Ber.*, **24**, 2298 (1891).

[148] Liebermann, C., *Ber.*, **23**, 142 (1890).

[149] Wislicenus, J., *Ann.*, **272**, 19 (1893).

Petroleum ethers of different boiling points have considerably different solvent powers. For example, Tiemann and Krüger[150] found that dimethyl-homo-phthalimide could be recrystallized only from petroleum ether boiling at 60 to 80°, while it was insoluble in lower boiling ligroin. Probably the solvent power of the petroleum ether increases in general with rise in boiling point. Toluene dissolves most materials better than does benzene, and in this respect, the relations between homologues should have the same influence on both the aliphatic and aromatic hydrocarbons.

The impurities present in petroleum ether may have a very harmful effect upon crystallizations. This is evident from the findings of Nölting and Schwarz,[151] who dissolved crude triquinylmethane in the smallest possible quantity of benzene, and then added ligroin, boiling below 100°, to the solution. However, they found it necessary to use ligroin that had been purified by treatment with sulfuric acid and then distilled, since the commercial product produced nothing but smears. As soon as the precipitate produced by the petroleum ether which was added in portions, no longer appeared gummy, they filtered and then added a little more ligroin, and allowed the product to crystallize adjacent to paraffin and sulfuric acid in a vacuum.

Phenol is an excellent solvent for many materials and is used far too little for crystallizing. For example, Witt[152] used it in the following way for crystallizing eurhodol which is insoluble in all other known solvents. He dissolved the hydrochloride of the base in phenol, cooled the solution to 100°, and then added boiling alcohol, to which a very little aniline had been added. The aniline combined with the hydrochloric acid present and the crystalline eurhodol began to separate as needles. This is the first instance in which an organic base has been used in place of ammonia, potassium hydroxide or sodium hydroxide, which are commonly the only materials used in such cases.

Phenol may separate as phenol of crystallization, as has been observed, for instance, with urea[153] and with cholalic acid.[154] Nitroso-dimethyl aniline[155] separates with $\frac{1}{2}$ molecule of phenol of crystallization, which is completely driven off by long heating even at 70°. Hexa-methylene tetramine crystallizes[156] with 3 molecules of phenol, $C_6H_{12}N_4+3C_6H_5OH$.

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[150] Tiemann, Ferd and Krüger, Paul, *Ber.*, **26**, 2687 (1893).

[151] Nölting, E., and Schwarz, Ch., *Ber.*, **24**, 1606 (1891).

[152] Witt, Otto N., *Ber.*, **19**, 2791 (1886).

[153] Eckenroth, H., *Arch. Pharm.*, **224**, 625 (1886).

[154] Latschinoff, P., *Ber.*, **20**, 3278 (1887).

The phenol adhering to the crystals after draining off the mother liquor may be removed by washing with alcohol.

PYRIDINE, CARBON BISULFIDE, TOLUENE

Pyridine, a very useful crystallizing medium is, for instance, according to Böttiger,[157] particularly suited for recrystallizing chlorinated benzidine and tolidine derivatives which are hardly soluble in other solvents.

The purification and optical investigation of osazones is often made more difficult because of their slight solubility in the ordinary solvents. According to Neuberg,[158] this difficulty is obviated in most cases by using pyridine as a solvent. Solubility in pyridine appears to be a general characteristic of all osazones; *e.g.*, 1 gram of pyridine dissolves about 0.25 gram of phenylglucosazone in the cold, and about 0.6 gram at its boiling point. Because of this considerable solubility, and because the solutions frequently tend to supersaturate, the direct crystallization of small quantities from pure pyridine is not possible; but these compounds may be purified in the following way. Even a slight addition of pyridine greatly increases the solubility of osazones in all the solvents likely to be considered, such as water, alcohol, carbon bisulfide, benzene, acetic ester, chloroform, etc., and by using suitable mixtures, the most favorable conditions for recrystallizing even the most difficultly soluble osazones may be easily established. The hydrazones and hydrazides behave the same in every particular. The marked ability of pyridine to take up osazones suggests its use as a solvent for these compounds when investigating their optical behavior toward polarized light. The conditions are particularly favorable in the case of osazones purified with pyridine, especially those precipitated by water and ligroin, which are characterized by clear shades of color. However, Neuberg found that solutions in pure pyridine do not always manifest the maximum rotation.

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[155] Schraube, Conrad, *Ber.*, **8**, 618 (1875).

[156] Moschatos, H., and Tollens, B., *Ann.*, **272**, 280 (1893).

[157] Böttiger, Edward, Dissertation, Jena, 1891.

[158] Neuberg, Carl, *Ber.*, **32**, 3384 (1899); *Ber.*, **35**, 2631 (1902).

Carbon bisulfide is a very useful crystallizing medium in many cases. Arctowski[159] has tested the various methods proposed for the purification of carbon bisulfide and he finally adopted Sidot's[160] method. It consists simply of shaking carbon bisulfide thoroughly with mercury, and then distilling. If these operations are carried out conscientiously it is easy to obtain a product of absolute purity. Consequently, it is better to shake small quantities of the liquid with rather considerable amounts of mercury in a vessel only half filled. The shaking must be continued until all the strong ethereal odor has disappeared. After decanting, the turbid liquid is slowly distilled. The product thus obtained cannot be preserved for long in large quantities, even over mercury and protected from light and air, because decomposition always sets in anew. It is better to purify a new supply when needed.

In very rare instances carbon bisulfide is not an indifferent solvent but takes part in the reaction. Such a case is encountered during the action of bromine on dry sodium malonic ester suspended in carbon bisulfide. There is obtained, with formation of sulfur bromide, a sulfur derivative instead of ethylene tetra carboxylic ester, as is shown by the equation:[161]

$$2\ C_7H_{11}O_4Na + 2\ CS_2 + 2\ Br_2 = C_{16}H_{22}S_3O_8 + 2\ NaBr + SBr_2$$

The reaction proceeds normally if iodine is used in place of bromine.

It has been mentioned that toluene dissolves many materials. Staedel[162] has found that even the purest commercial product often gives rise to smeary products. This characteristic is lost if the toluene, before being used, is shaken several times with concentrated hydrochloric acid and then several times more with a little sulfuric acid, and then washed with water, dried and distilled. This treatment removes any pyrrol and thiotolene.

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[159] Arctowski, H., *Z. anorg. Ch.*, **6**, 257 (1894).

[160] Sidot, Th., *C. r.*, **69**, 1303 (1869).

[161] Wenzel, G., *Ber.*, **33**, 2041 (1900).

[162] Staedel, W., *Ann.*, **283**, 165 (1894).

LIQUID SULFUR DIOXIDE, LIQUID AMMONIA

Purification of anthracene

If, concluding the discussion of solvents suitable for crystallization, details concerning liquid sulfur dioxide and ammonia and of the purification of anthracene are included, the reasons are as follows:

This volume is not designed as a text book giving directions for several preparations suitable for beginners; very good compilations of this kind are rather numerous. It aims to deal not with a single case which has been investigated but rather to point the way toward more easily accomplishing a desired result by suitably applying and especially by intelligently modifying known facts. The investigator who might be without certain knowledge in this particular field would not need to start at the beginning because it is not possible in a given case to always find the pertinent facts in the literature, as these occasionally are contained in articles which have absolutely no connection with the problem at hand. In addition, the patent literature is very slightly known, even today, in very many scientific laboratories. It is obvious that it must contain much excellent material. A number of chemical reactions are repeated daily, even many times daily, and on the largest scale in the factories. A considerable number of the best trained chemists constantly observe chemical reactions which seem susceptible of improvements whose discovery would often be extremely profitable. They sometimes use means which would hardly be employed in purely scientific laboratories, although later they might be of the greatest value even to these, because in the laboratories, time and cost are usually not of prime importance and, in any case, are not the decisive factor. If the development leading to the gradual perfection of such working methods is followed by means of the patents pertaining thereto, it may be the source of much inspiration. Other cases of this kind may be encountered, but here, where the opportunity is offered for the first time to follow a comparatively simple course of the practical development of a working method, it seems proper to give the reasons why the writer has taken up the historical development of such individual methods in their entire chronological order.

There is no particular difficulty in completely purifying a few grams of anthracene, $C_{14}H_{10}$, in the laboratory. But it is entirely different in technical practice, where thousands of kilos of it are handled, which later is to be transformed into alizarin or, more recently, into many other valuable dyes. The earlier customary procedures were not studied in detail, and they probably did not differ very much from those taken over from the scientific laboratory. Besides, every manufacturer had every reason to keep for himself the experience which he had often obtained at the expense of much patience and not to make this known to others, as long as he had no patent protection, or if patenting of the process seemed to offer no protection. On the other hand, the patenting of a process reveals much that otherwise would have remained secreted in the factories. It might be said that these patents relieve the discoverer of the care of keeping the secret and make the process an open secret for a period of years. This common knowledge, however, cannot be used, during the life of the patent, to the detriment of the discoverer.

Crude anthracene as separated directly from the high boiling portions of tar oils, in solid crystalline masses contains a large number of foreign organic compounds which more or less interfere with its being used for the preparation of alizarin and related dyes. A part of the impurities may be removed with comparative ease by recrystallization from benzene, ligroin, alcohol and similar solvents, *i.e.*, the crude anthracene may be enriched in so far as certain of the contaminants are much more soluble in the media named than it is. This method of enrichment leads to a really high percentage antharcene only at the expense of considerable loss. It is still worse that such anthracene still contains its most troublesome impurity, carbazole, $(C_6H_4)_2>NH$, first observed by Gräbe,[163] because it is just as little soluble in all the usual solvents as is anthracene. The most certain method of removing the carbazole was to distil the crude anthracene over caustic potash, which retained the carbazole since it, as an imide, combines with the potash to form a potassium salt. This method was rather inconvenient and expensive, and the search for a crystallizing medium in which the carbazole would remain dissolved, while the anthracene separated, appeared to be a profitable problem.

Remy and Erhart[164] believed that oleic acid, a rather uncommon medium, was the right solvent. They purified anthracene with oleic acid in the following way: 100 kgm. of crude anthracene was added to 150 kgm. oleic acid heated to 110 to 120°, with constant stirring, until almost all was dissolved. When the solution had cooled, all of the anthracene present had separated in crystalline form, together with comparatively small quantities of related compounds. The oleic acid containing the greater part of the impurities in solution was almost completely removed by filtration or centrifuging and pressing. The press cakes were freed of the last traces of the adhering oil by treatment with alkali, or by extraction with petroleum or other suitable liquids. The yellowish or greenish white, brittle powder remaining in both cases, was "purified anthracene."

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[163] Graebe, C., and Glaser, C., *Ann.*, **163**, 343 (1872).

[164] Remy and Erhart, German patent 38417 (1886); Fr. I, 304.

However, the results with oleic acid could not have been entirely satisfactory because soon after, the fact that all the companions of crude anthracene, including carbazole, are much more soluble in the pyridine, quinoline and aniline bases than is anthracene itself, was pointed out as being of value for this purpose. In this way, one single act of solution was supposed to produce directly, not only high percentage anthracene, but anthracene practically free of carbazole and its homologs. The crude pyridine bases produced in the distillation of coal tar are best for this purpose. They are used in the following way: 1 part of crude anthracene and 1.5 to 2 parts of these bases are placed in a kettle provided with a stirrer, heated in a water or steam bath, and the materials stirred until the solid has dissolved. After the solution has cooled, the anthracene which has crystallized out, is separated from the mother liquor by filtration, pressing or centrifuging. A crude 33 per cent anthracene yielded one of 82.5 per cent after this treatment.[165]

In 1892[166] it was found that sulfur dioxide could be advantageously used for purifying crude anthracene as well as technical anthraquinone. This involved a crystallizing agent never used before. While the other materials present in crude anthracene are, for the most part, soluble in liquid sulfur dioxide, anthracene itself is taken up only slightly by this solvent. Analogously, the accompanying materials in technical anthraquinone are comparatively soluble in sulfur dioxide, and anthraquinone is almost insoluble in it.

For instance, if a crude product containing 30 per cent of anthra cene is covered with its weight of liquid sulfur dioxide, and then filtered, almost half of the crude anthracene dissolves. The filtration residue, analyzed after evaporation of the sulfur dioxide, showed about 50 per cent of anthracene. After the sulfur dioxide was driven from the filtrate, the residue contained only about 2 per cent of anthracene.

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[165] Ch. Fab. A-G., German patent 42053 (1887); Fr. I, 305.

[166] Bayer & Co., German patent 68474 (1892); Fr. III, 194.

Results were much more favorable when a larger excess of sulfur dioxide was used. Under these conditions, not much more anthracene dissolves but the percentage content of purified anthracene rises. For instance, 70 to 80 per cent anthracene resulted from the use of four times the quantity of sulfur dioxide.

The following comparative experiment may be used in the laboratory to show the preceding results and also that the use of sulfur dioxide is not too complicated. If 100 grams crude anthracene, for instance, in an ordinary flask is covered with 400 grams liquid sulfur dioxide, the mass may be easily shaken together under a hood, and then poured on to a suction filter, because the sulfur dioxide is so well cooled by the evaporation that considerable time elapses before much of it evaporates. Under these conditions, the liquid boils gently, and there is no necessity for particular haste, nor is there any other difficulty in completing the mixing, stirring and filtering. The purified anthracene remains on the filter, while the impurities are almost exclusively in the mother liquor.

The process is carried out on a large scale as follows: The liquid sulfur dioxide is forced into wrought iron reservoirs from the cylinders containing 500 to 1000 kgm. as furnished to the trade. At summer temperatures, the sulfur dioxide is under a pressure of 3 atmospheres in these riveted boiler-plate containers. Owing to the method of recovery, the pressure finally rises to 5 to 6 atmospheres. At the beginning of the operation 600 kgm. of crude anthracene is put through a man-hole into a wrought iron cylinder provided with a stirrer, and after the cover is fastened on, 2400 kgm. of sulfur dioxide is pumped in, the air escaping from the kettle being sucked off at a corresponding rate to recover the sulfur dioxide contained in it. After a short stirring, the sulfur dioxide has dissolved the impurities. Together with the anthracene, it is forced by its own pressure into an iron filter tower in which the purified anthracene remains on the filter, while the mother liquor is driven into an adjacent kettle. The filter tower is surrounded by a steam jacket so that the sulfur dioxide remaining in the purified anthracene may be driven off by heat. The mother liquor is warmed by a steam jacket surrounding the kettle in which it was collected. The sulfur dioxide boils off easily and completely and the residue, melting below 100° and containing only a few per cent of anthracene, is run off as valueless. The sulfur dioxide which has gasified during these various operations is passed through a copper coil cooled with water, and then through the bronze cylinder of a compression pump, so that it is constantly returned as a liquid to the storage vessels.

The purification of anthraquinone may be carried out in the same way. If it is treated, for instance, with 4 times its weight of sulfur dioxide, the accompanying materials which are harmful in the subsequent use, are easily dissolved, while not so much as 1 per cent of the anthraquinone goes into solution.

While liquefied gases are suited to the purification of crude anthracene, it is not necessary that the gas be liquid sulfur dioxide. Wilton[167] found that liquid ammonia also dissolved most of the impurities of anthracene, while this material itself is practically insoluble in it. The liquid ammonia is allowed to pass through the anthracene several times under 9 atmospheres pressure. Comparatively pure anthracene remains behind, while the selective action of the solvent removes the impurities.

Another patent[168] claims that acetone particularly (even crude acetone or homologous ketones of the acetone group) may be used to purify anthracene. If this holds in general, it is rather remarkable that it was discovered so late. The directions for this method of purification are given for the sake of completeness: 560 kgm. of crude anthracene, for instance, is stirred with 750 kgm. of acetone in a closed cylinder, provided with a stirrer, and surrounded by a steam jacket. The mass is then heated to 60° and kept at this temperature for an hour. It is then allowed to cool, the anthracene filtered off and washed with 375 kgm. of the solvent. The acetone for washing is collected separately, and used for a new purification process. The acetone is recovered from the first mother liquors by distillation. The anthracene remaining on the filter is pressed and dried. It is claimed that 82 per cent anthracene is easily obtained from 35 per cent crude anthracene, while the residue from the distillation of the mother liquors contains only a few per cent.

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[167] Wilton, Thos., German patent 113291 (1899); Fr. VI, 47.

[168] Bayer & Co., German patent 78861 (1894); Fr. IV, 270.

According to Luyten,[169] the crude oil from which anthracene crystallizes has a particularly strong solvent action on the accompanying impurities. If this crude oil is then added to the ordinary solvents such as acetone, benzene, pyridine, etc., usually used for extracting the impurities from crude anthracene, it is claimed this mixed solvent yields a particularly pure anthracene, since it extracts the impurities much better than the above-mentioned solvents alone.

The following additional process designed to recover high percentage anthracene in an entirely different manner, was patented.[170] According to it, the greater part of the phenanthrene is first removed from the crude anthracene by melting and partial crystallization. Very exact statements as to the success of this partial crystallization are given in a French patent.[171] The carbazole is then removed by treatment with caustic potash at a definite temperature, and finally the rest of the phenanthrene is removed by means of benzene. The anthracene is melted, transferred to a well insulated metal kettle holding 2000 kgm., and allowed to cool slowly. After about 50 per cent of the mass has crystallized, the exit at the bottom is opened and all of the liquid is run off into a similarly arranged vessel, in which an additional large part of the anthracene may be recovered by repeated partial cooling and crystallization. The crop of crystals II, with lower anthracene content, is enriched by renewed melting, as was crop I, first obtained, whose anthracene content was about 45 to 50 per cent. Crop I is put into a cast iron vessel fitted with a stirrer, melted, the stirrer started and 50 per cent caustic potash allowed to flow into the mass heated a little above its melting point, but not over 260°. The quantity of alkali is regulated by a determination of the carbazole content of the crystals. The melt separates into two layers; the lower one of mobile, fused potassium salt of carbazole is drawn off through the cock at the bottom of the fusion vessel. The anthracene layer is then run into a vessel placed between the melting pot and the solution apparatus, and is cooled to just a little above the melting point of the anthracene. It is then transferred to a solution apparatus provided with a stirrer and a reflux condenser. This vessel contains an equal weight of benzene. It is best if this is the so-called 90 per cent benzene of commerce. Benzene dissolves the phenanthrene still remaining in the anthracene, while the latter does not dissolve, and after pressing or centrifuging, it is obtained as a fine, light, brown powder containing about 90 per cent pure anthracene. This is another example of the use of potassium hydroxide as a means of removing carbazole. Thus this method used for a long time in the laboratory and which the preceding patents all tried to eliminate, has again come in vogue, although in a modified form.

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[169] Luyten, Louis, German patent 141186 (1900); Fr. VII, 159.

[170] A-G. f. Teer- und Erdöl-Industrie, German patent 111359 (1899); Fr. VI, 46.

[171] Scholvien, L., French patent 335013 (1903); *Chem. Zeit.*, **28**, 308 (1904).

For the sake of completeness,—the process hardly comes within the compass of this heading,—it should be mentioned that Wirth[172] recommended that carbazole and its homologues be removed by treating a hot solution or a suspension of crude anthracene in an indifferent solvent with nitrous acid. The nitroso compounds of carbazole and its homologues formed, either go into or stay in solution, while carbazole-free, high percentage anthracene remains behind or separates on cooling.

RECOVERY OF THE CRYSTALS FROM SOLUTIONS AND MOTHER LIQUORS; RECRYSTALLIZATION

As mentioned in the introduction to this section, it is general practice to allow hot saturated solutions to cool slowly to obtain crystals from them. Frequently, a second liquid is added to the solution after filtering it, and this mixes with the solvent, but the material to crystallize is insoluble or hardly soluble in it. The addition of the precipitating agent is usually stopped when the solution begins to be turbid. The turbidity may be cleared easily by renewed addition of the true solvent, and thus an abundant crystallization may be obtained from the clear solution. Ordinarily, it is not necessary to remove the turbidity. If this procedure is applied to a hot solution, usually on cooling, practically all of the material which was dissolved will be transformed to the crystalline condition.

The art of crystallizing materials which are soluble in water, but insoluble in alcohol, and which could hardly be crystallized from any other solvent, was remarkably extended by Rümpler[173] in 1900. He dissolved such materials in water and added enough alcohol to make the solution turbid. The turbidity was filtered off or cleared up by the addition of a few drops of water. The clear solution was then placed in a desiccator which was charged, not with sulfuric acid, but with quick lime. Since the lime only absorbs the water from the solution, this constantly becomes richer in alcohol and a proportional precipitation of the dissolved material ensues. Because of the slowness of the process, the separation occurs in the crystalline form if the material in question is at all capable of crystallizing. In this way, he obtained crystals of glue peptone, albumin peptone, and also of arabinic acid. The writer has used this method with excellent results.

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[172] Wirth, Ernst, German patent 122852 (1900), Fr. VI, 48; R. Wedekind & Co., German patent 167743 (1904), Fr. VIII, 273; R. Wedekind & Co., German patent 172300 (1904), Fr. VIII, 274.

Petroleum ether is frequently added to ether solutions, since many materials are soluble in ether, and practically insoluble in petroleum ether. It is often an advantage to add alcohol to phenol solutions,[174] etc.

A pertinent procedure, capable of many variations, and leading to success in rather difficult cases was communicated to the writer by Klinger. It serves for materials rather difficultly soluble in benzene, but more soluble in benzene on the addition of alcohol, and which can hardly be crystallized in any other way. Frequently, it is only necessary to shake the crystallizing mixture with water, to obtain the result desired. Since the alcohol is in this way washed out of the benzene, and the latter can no longer hold the dissolved material in solution, the solute frequently separates immediately as crystals. Thus, Türkheimer[175] suspended 100 grams of crude diphenyl-glycollic acid in 100 grams of benzene, warmed, and added, with further cautious warming, 60 cc. of alcohol, which was just enough to complete solution. The solution, while still hot, was filtered into a separatory funnel of the proper size which contained 200 cc. warm water. Then 800 cc. of warm water was added, which sufficed to precipitate the acid from the benzene-alcohol solution. The alcohol was extracted from the solution by the water, and the acid, thus deprived of its solvent, precipitated in a pure white condition, while the impurities remained dissolved in the benzene. The crystallized acid was filtered off after the system had been allowed to stand for about a day.

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[173] Rümpler, A., *Ber.*, **33**, 3474 (1900).

[174] Witt, Otto, *Ber.*, **19**, 2792 (1886).

[175] Türkheimer, Dissertation, Königsberg, 1904.

A private communication from Klinger states that the miscibility of ether with concentrated hydrochloric acid may render good service in obtaining materials otherwise difficult to crystallize. For instance, benzophenone is obtained in beautiful crystals if its ether solution is mixed with concentrated hydrochloric acid. Everything should stay in solution, and the solution is allowed to stand in a wide test tube. As the ether continues to evaporate, the crystal formation of the ketone gradually increases.

The separation of crystals from solvents is often initiated, or very much assisted, by rubbing the walls of the vessel with a glass rod. Solutions of creatinine-zinc chloride constitute a well known example of this. If an alcoholic zinc chloride solution is added to an alcoholic solution of creatinine, the salt does not separate, even after long standing, although it is not soluble in alcohol. If the walls of the vessel are rubbed slightly, the separation is complete after 24 hours. On one occasion, the writer filtered a solution of the double salt that had stood for 3 weeks, at temperatures as low as −15°, believing that everything had crystallized from this solution, which was capable of yielding 30 grams. But in the course of several hours, at room temperature, the mother liquor deposited the remaining 10 grams; the agitation during filtration caused this.

In general, liquids are allowed to cool completely to obtain a larger yield of crystals, indeed, as mentioned above, they are strongly cooled on purpose. There are only a few exceptions to this rule, but these rare cases are of great importance. Thus, crystallized veratrine is only obtained certainly, and in good yield if, according to Schmidt and Bosetti,[176] the commercial alkaloid purified by ether is dissolved in absolute alcohol in a large beaker, the solution heated to 60 to 70°, and enough water added to produce a permanent turbidity. If this is cleared by the addition of alcohol, and then allowed to evaporate at 50 to 60°, considerable quantities of practically pure crystalline veratrine separate. However, as soon as the liquid begins to be turbid, because of the separation of the gummy modification of veratrine, it must be poured away from the crystals as rapidly as possible. The whole operation can be repeated several times with it, and thus, up to 33 per cent of the commercial base may be transformed to the crystalline condition.

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[176] Bosetti, E., *Arch. Pharm.*, [3], **21**, 84 (1883).

Kiliani[177] has shown that the preparation of crystallized digitalin is particularly difficult. These obstacles cannot be recounted in abstract, while their discussion in extenso would require too much space.

It is customary to wash crystals to remove the adhering mother liquor. When dealing with larger quantities, they are filtered with suction. It is better to close the funnel with a glass marble, instead of with a platinum cone, either with or without paper, especially if the mother liquor is strongly acid or alkaline. According to Witt,[178] high-speed centrifuges, provided with baskets of pure nickel which is not attacked by acids, should be used when separating crystals from very strongly acid liquids.

If there are only a few crystals, they are spread on unglazed porcelain, in case the mother liquor is very thick, but if the porcelain is not available, bricks which absorb the mother liquor may be used. If the crystals are pressed between filter paper, the results are usually not so good as with the plates. In case the mother liquor is valuable, it may be recovered by extracting the paper.

As is well known, crystals may be identified crystallographically as well as by analysis. Indeed, since the analytical figures for all compounds having the same empirical formula are identical, isomeric compounds, etc., cannot be distinguished from each other more surely than by crystallographic investigation. The crystals to be measured should not be too large, so that they may be conveniently fastened on the reflection goniometer, but they must have smooth, well reflecting surfaces and sharp angles.

Mother liquors usually deliver additional crystals after being concentrated and then cooled. Of course, they may be treated to turbidity by suitable agents to avoid the evaporation, or the two methods may be combined. According to Weitenkampf,[179] materials dissolved in alcohol, ether, or chloroform, may be precipitated without evaporating or adding anything, if the solutions are strongly cooled, and at the same time saturated with carbon dioxide at a pressure of 3 atmospheres. This process is only valuable for technical purposes, because no method requiring such apparatus would be favored in the laboratory.

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[177] Kiliani, H., *Arch. Pharm.*, **233**, 302 (1895); *Arch. Pharm.*, **234**, 481 (1896).

[178] Witt, Otto N., *Ber.*, **48**, 754 (1915).

[179] Weitenkampf, C., German patent 57393 (1890), *Ber.*, **25**, R 88 (1892); German patent 69884 (1892), *Ber.*, **26**, R 900 (1893).

The purpose of any crystallization is to prepare the compound in question in the state of the highest possible chemical purity. If this cannot be done in one operation, the recrystallization is repeated until the result is achieved, and all impurities remain in the mother liquors. How this may be determined will be evident from the work of Schwalb, to be given later.

It is assumed, when purifying by recrystallization, that mixtures of crystallizing substances may be separated because of differing solubility in a suitably chosen crystallizing medium; consequently, if the quantity of solvent is correctly chosen, more of one of the materials than of the other will remain in the mother liquor. In fact, practically the only mixtures of crystals which could not be separated by fractional crystallization were observed among the thiophene derivatives. Cohn[180] has made the interesting discovery that if molecular quantities of *p*-nitrobenzoic acid and *p*-acetylaminobenzoic acid are dissolved in hot water, they crystallize out together, on cooling, and it is impossible to decompose the double compound by subsequent crystallization, or even by fractional precipitation of the silver salts. Similar behavior of mixtures of other acids have previously been reported by Hlasiwetz and Barth,[181] as well as by Kolbe and Lautemann.[182]

Mixed crystals in the ordinary sense are often mentioned. Thus Herrmann[183] found that succinylosuccinic ester which crystallizes asymmetrically, and quinone-dihydro-dicarboxylic ester which crystallizes rhombically, form mixed crystals. However, the labile asymmetric hydroquinone-dicarboxylic ester which is desmotropically isomeric with the quinone-dihydrodicarboxylic ester does not form such mixed crystals.[184]

It has long been known that materials which separate as oils may be made to crystallize as the result of "crystal seeding,"[185] if they are touched with a crystal of the same material obtained from a previous preparation. Thus in 1854, Williamson and Scrugham[186] recommended that carbolic acid be recovered from coal tar by adding several phenol crystals to the distillate which had passed over between 186 and 188°, and this produced a copious separation of crystals. The aldoximes, according to Bourgeois and Dambmann[187] belong to the materials which are particularly prone to separate as oils, since even very small quantities of adhering impurities hinder their crystallization.

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[180] Cohn, R., *Ber.*, **25**, 2465 (1892).

[181] Hlasiwetz, H., and Barth, L., *Ann.*, **134**, 276 (1865).

[182] Kolbe, H., and Lautemann, E., *Ann.*, **119**, 139 (1861).

[183] Herrmann, F., *Ber.*, **19**, 2235 (1886).

[184] Hantzsch, A., and Herrmann, F., *Ber.*, **20**, 2810 (1887).

Staedel has now found that a crystal of the same kind is not always essential, but in many cases, a seed of one of similar chemical constitution suffices to start the crystallization. Thus he succeeded in crystallizing *m*-cresol which was held to be uncrystallizable[188] and which was said not to solidify at $-80°$, by dropping a tiny crystal of phenol into the *m*-cresol after cooling it to $-18°$. Ott[189] reports that propylidene-acetic acid dibromide which would not crystallize, soon became solid when he seeded it with a small crystal of ethylidene-propionic acid dibromide. A third instance, is the observation of Green,[190] who after many attempts, succeeded in crystallizing methenyl-di-*p*-toyl-triamino-toluene from petroleum ether, only after dropping a crystal of the more readily crystallizing homologous ethenyl compound into the solution.

The behavior of nitroglycerol is reminiscent of crystal inoculation, because it (glycerol trinitrate) does not readily crystallize, but it is easily obtained as a solid if kieselguhr[191] is added to a portion which is then cooled several times from 0° to $-20°$. If the main quantity is later inoculated with the solidified portion, it also solidifies rapidly. Crystallized glycerol di- and mono-nitrate may be obtained in the same way. Claessen[192] claims that dinitroglycerol does not crystallize well unless it contains some moisture. Consequently, his procedure is to allow a small quantity of dinitroglycerol to stand for two hours in an atmosphere containing 75 to 85 per cent of moisture, and then knead it to a dynamite-like mass with kieselguhr. The mass is placed in a freezing mixture and kept there, until after frequent rubbing with a glass rod, it suddenly solidifies to a hard, crumbling mass. The compound $3C_3H_5(OH)(NO_3)_2+H_2O$, free of all impurities is obtained by recrystallization from a little water.

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[185] Salkowski, E., *Z. physiol. Ch.*, **10**, 151 (1886).

[186] Williamson, A., and Scrugham, *Proc. Royal Soc.*, **7**, 18 (1854).

[187] Bourgeois, Ed., and Dambmann, J., *Ber.*, **26**, 2856 (1893).

[188] m-Cresol is now commercially available which readily solidifies in an ice-salt bath and then melts at 10°.—H. T. C.

[189] Ott, P., *Ber.*, **24**, 2603 (1891); Staedel, W., *Ber.*, **18**, 3443 (1885).

[190] Green, Arthur G., *Ber.*, **26**, 2778 (1893).

[191] Will, W., *Ber.*, **41**, 1112 (1908).

[192] Claessen, C., German patent 210990 (1907); *Chem. Zentr.*, **80**, II, 248 (1909).

In many cases, chemically pure materials can only be obtained by frequently repeated crystallizations directed in a definite sense. This procedure is called fractional crystallization. An example will best show the manner in which, mutatis mutandis, the procedure should be carried out.

Schwalb[193] saponified beeswax with sodium hydroxide and extracted the dry soap with petroleum ether. The resulting non-acid products of saponification of the wax were subjected to a systematic fractional crystallization carried out as follows: The highest melting fractions were recrystallized from pure petroleum ether, while the mother liquor of the preceding higher melting material was always used for recrystallizing the lower melting products. In this way, the low melting materials accumulated in the last mother liquors, while the highest melting components were found in the first crystallizations. This systematic recrystallization was continued until the mother liquor, from the crystals separating on cooling, gave on evaporation of the petroleum ether, a product whose melting point was not essentially different from that of the crystals first obtained. As soon as this point was reached, this crystallization was set aside for further working up; and the recrystallization of the intermediate products, which had not been purified as far, was continued. Thus, three main portions were first obtained, which in their turn, were further treated in the same way. In this manner, besides many other products, one material was obtained whose analysis indicated a hydrocarbon. It was necessary to recrystallize this product alone, thirteen times, until the melting point of the crystals and of the residue obtained by evaporation of the mother liquor, agreed.

It should not be overlooked that all the impurities of the crystallizing medium, that is, of the alcohol, ether, petroleum ether, etc., accumulate in the evaporation residue of the mother liquor, and these will depress its melting point. Consequently, it is necessary to purify the solvent by distillation shortly before using, to remove all non-volatile residue from it so that there may be no doubt of this infallible test, that compounds have been purified by recrystallization. The writer[194] proceeded in this way, for example, in his study of the action of hypohalogenites on dipotassium salicylate solutions, and concluded that it is entirely impossible to prepare any (*i.e.*, say, other isomeric) chloro-,bromo-, or iodo-salicylic acids, other than those described, by means of halogenites.

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[193] Schwalb, Fr., *Ann.*, **235**, 110 (1886).

When dealing with crystallized bodies which cannot be identified by the melting point, it is perhaps possible to use Zinoffsky's procedure, or it may be possible for the operator to devise a corresponding method for the case at hand. Zinoffsky[195] could only be certain that the oxyhemoglobin of horse blood, purified by recrystallization, was actually a uniform material by determining that the iron content of the dried residue of the mother liquor was the same as that of the dried crystals.

In addition, the following may be noted. It is not particularly difficult to obtain crystalline oxyhemoglobin from the blood of the horse, the dog, or many other animals, but on the contrary, considerable trouble is encountered with the blood from many other species. This is true of swine blood. Hüfner,[196] however, made the remarkable observation that this blood, when freshly defibrinated, if treated directly with one-third part of approximately one per cent alcoholic solution of quinoline, and then allowed to stand in a freezing mixture, is after several days, converted into a thick red crystal magma of oxyhemoglobin. Otto continued the work along this line.

If materials are obtained which cannot be recrystallized by any means, attempts must be made to produce them directly in the highest possible state of purity for analysis, by starting with very pure materials. Herth[197] did this, for example in the synthesis of biguanid. It is obvious that rules of general applicability for such cases cannot be set up, as a special method must be used in each particular case.

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[194] Lassar-Cohn, and Schultze, Fritz, *Ber.*, **38**, 3294 (1905).

[195] Zinoffsky, Dissertation, Dorpat, 1885.

[196] Otto, J., and Hüfner, G., *Z. physiol. Ch.*, **7**, 57 (1882).

[197] Herth, R., *Monatsh.*, **1**, 89 (1880).

CRYSTALLIZATION OF CLOSELY RELATED DERIVATIVES

The foregoing is sufficient to show the care and thought that must be exercised by the synthetic organic chemist when he endeavors to crystallize his new preparations. To be frank, it must be admitted that up to the present, the organic chemist was only certain of his ground when working with such compounds as were volatile without decomposition, or which could be obtained crystalline or at least in the form of a closely related crystalline derivative. To this list may be added careful fractional precipitation,[198] as a third reliable procedure.

It is only seldom that a closely related derivative of a compound is as readily available as it was to Liebermann and Limpach,[199] when they found themselves unable to obtain mandelic anhydride in a form pure enough for analysis. They established its nature by converting it into a mandelate by boiling with dilute alkali. Purification of difficultly crystallizable materials, or their separation from mixtures containing other constituents which hinder their crystallization, by converting them into closely related, easily crystallizable compounds by acetylation, benzoylation, etc., has now been highly perfected.

SALTING OUT

Many solid materials, and also some liquids can be recovered from their aqueous solutions, not only by evaporating the water, or by crystallization, but also by so modifying the solvent by the addition of other materials, that it no longer can dissolve them. From ancient times, sodium chloride has been added for this purpose, and consequently, the whole procedure is briefly termed "salting out."

The oldest application is in the soap industry, in which, before the days of soda, common salt served to convert potassium soaps prepared from potash, into the hard sodium soaps which are so slightly soluble in brine that they later float on the bottom lye. In this case, besides salting out, it also takes part in the process because of its sodium content. It behaves similarly in its second oldest application. In 1740, a Saxon dyer, Barth, discovered the solubility of indigo in fuming sulfuric acid, and also the solubility of the new dye in water, in contrast to indigo itself. To recover the new dye in the solid form, from its solution, he added considerable salt to the liquid, and thus salted out the indigo carmine (sodium salt of indigo disulfonic acid) which is easily soluble in pure water, but scarcely soluble in salt water.

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[198] Berdez, J., and Nencki, M., *Arch. Path. u. Pharm.*, **20**, 351. (1886).

[199] Liebermann, C., and Limpach, Ludw., *Ber.*, **25**, 931 (1892).

The salting out of dyes was introduced into the aniline dye industry very early. As long ago as 1859, fuchsine was salted out of its solutions, and at present, a great number of dyes are separated in the solid form in this way.

Of course this action is not limited to sodium chloride, it may even be increased by the addition of salts still more soluble, thus for example, zinc chloride may be used along with sodium chloride. Or more soluble salts such as potassium chloride may be employed from the start. Glauber's salt is also much used. The very soluble potassium carbonate is able to even cause the alcohol to separate from alcoholic solutions, forming an upper layer if enough of the salt is added. If the nature of a water solution will permit the addition of potassium carbonate, the solution may be directly shaken out with alcohol after the addition of sufficient potassium carbonate (see page 18). Fractional salting out is also useful, as for example, when precipitating smeary impurities from liquids by moderate addition of salts. Only then are the liquids acidified or made alkaline and extracted with ether. In this way, the acid[200] or base is obtained directly in a comparatively pure condition.

Also, hot solutions[201] may be precipitated with hot salt water, since sodium chloride is about equally soluble in hot or cold water. The non-crystallizing zinc chloride could also be used for this purpose, but potassium chloride, for instance, would not be suitable.

In this way, separations may be carried out which are particularly important in the chemistry of albumins. Thus ammonium sulfate may serve in the separation of albumins from peptones and albumoses. (These are the derivatives of albumin which are modified, for example, by digestion or by sulfurous acid, and which are no longer coagulable by boiling water.) Only true albumins are insoluble in a solution saturated with this salt, and consequently they precipitate when this is added.[202] Such separations, which play an almost decisive rôle in the chemistry of albumins, are regarded by many as quantitative, but there is no certain evidence to support this view. Thus it is claimed that the water-soluble mixture of albumose and peptones[203] prepared from albuminous materials of any desired origin, by the action of enzymes, acids, alkalis, as well as by superheating with water, may be obtained entirely free of albumose if a dilute solution of this mixture is saturated with ammonium sulfate in neutral, alkaline and acid solution in turn, at the boiling temperature, followed by cooling. The separation of the albumose by ammonium sulfate, which is ordinarily incomplete, is said to be complete if carried out in this way.

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[200] Pinnow, J., and Pistor, G., *Ber.*, **26**, 1314 (1893).

[201] Baeyer, Adolf, *Ber.*, **12**, 1317 (1879).

[202] Kühne, W., and Chittenden, R., *J. Biol.*, **22**, 423 (1886).

On the other hand, salting out may, of course, be very useful if the precipitated substance, which perhaps can be prepared from the solution at hand in a pure condition only with difficulty by another method, can later be made uniform by recrystallization. Baeyer,[204] for instance, dissolved amino-indigo in dilute hydrochloric acid, neutralized with soda and recovered it from the solution by reprecipitating it with sodium acetate. He treated amino-phthalic ester[205] in the same way.

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[203] Farbwerke Meister Lucius, und Brüning, German patent 70281 (1892); *Chem. Zeit.*, **17**, 1290 (1893).

[204] Baeyer, A., *Ber.*, **12**, 1317 (1879).

[205] Baeyer, A., *Ber.*, **10**, 1079 (1877).

CHAPTER XIII

Solvents and Diluents

THE INFLUENCE OF SOLVENTS AND DILUENTS

If the rule, "Corpora non agunt nisi fluida," holds for chemistry in general, the following additional statement is valid for organic chemistry in particular: "The proper choice of solvents and diluents is essential to good yields." Innumerable investigations have suffered either because of ignorance or neglect of this rule, or have been ruined on this account.

The following examples will substantiate this statement. Attention therefore, should be directed to this point, which may seem so unimportant, before initiating reactions in the presence of solvents. Often there will be no difficulty in choosing the proper solvent. It is quite obvious that if a reaction proceeds best, at say 80°, that benzene will be a more suitable solvent or diluent than ether and so forth. However, the conditions are not always so simple.

Bucherer[1] obtained (a) only 1.5 grams of toluido-isobutyro-nitrile, when he mixed finely powdered *o*-toluidine hydrochloride (14 grams), potassium cyanide (7 grams) with acetone (5.8 grams) and 20 grams ether, shook and allowed to stand several days. (b) When he used the same materials with the exception that 30 grams ligroin was used in place of the ether, the mixture began to heat up at once. After evaporating the solvent, the residue was taken up in ether, and the hydrochloride precipitated with hydrogen chloride gas. The nitrile was obtained in the crystalline form by decomposing this salt with water. The yield in this case was 10 grams or 50 per cent of the theory. (c) A third lot in 30 grams benzene, yielded only 7 grams or 40 per cent of the theory.

Pummerer[2] found that benzyl-phenyl sulfide is oxidized in glacial acetic acid solution, rapidly and quantitatively to the sulfoxide by

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[1] Bucherer, H., and Grolée, André, *Ber.*, **39**, 994 (1906).

[2] Pummerer, Rudolf, *Ber.*, **43**, 1406 (1910).

30 per cent hydrogen peroxide, while the action is very slow in acetone solution. Since similar observations had already been made in this group by others,[3] certain solvents seem particularly suited for some groups.

It seems entirely superfluous to recall that the solute should have no chemical action on the solvent. This may occur unexpectedly, though not intentionally. For instance, chloroform is often used to dissolve phenylhydrazine. When such a solution is worked up, a small quantity of phenylhydrazine hydrochloride in well developed crystals, is obtained, even though the chloroform contained no acid. The reason for this has been given when discussing chloroform under the heading "Crystallization." This point has led to many errors, because phenylhydrazine is often used to detect very small quantities of other materials, by adding it to the solution obtained when attempting to extract these materials with chloroform.

Special reference should be accorded to the comprehensive studies of Menschutkin[4] and Pinner:[5] "The Influence of Indifferent Solvents on the Alkylation of Organic Bases."

SOLUTION AND EXTRACTION WITH COLD SOLVENTS

The solution or extraction of materials by cold solvents is best accomplished by using the principle that heavier liquids constantly sink to the bottom through lighter ones. This has already been applied to the emptying of sealed tubes containing adhering solids. An apparatus useful for the convenient and automatic dissolving of salts, the extraction of resins, etc., consists, according to Ubber, of a cylinder-like vessel with a turned over edge, having a ring of holes above, and ending below[6] in a narrow tube. This vessel *B* (fig. 131) fitted with a porcelain sieve, holds the material to be dissolved, and may be hung in any convenient receptacle, preferably a cylinder containing the solvent. The liquid passes through the small openings onto the material to be dissolved, takes part of it in solution, and the saturated solution sinks to the bottom through the narrow tube, while simultaneously, fresh solvent flows through the small openings in the upper part. If, in place of the straight walled cylinder, A, a very narrow one is used, whose upper shoulder is just wide enough so that the vessel B can still be conveniently admitted, comparatively little liquid will be required for the extraction. In this case, the vessel B is really not necessary, but a porcelain funnel with straight sides may be placed in the shoulder. A cock at the foot of the cylinder would provide a convenient means for drawing off the concentrated solution. The perforated porcelain plate prevents solid particles being carried along, and the solution being prepared may be filtered at the same time by putting in a plug of cotton, or of glass wool, or a disk of filter paper.

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[3] Hinsberg, O., *Ber.*, **43**, 289 (1910).

[4] Menschutkin, N., *Ber.*, **38**, 2465 (1905).

[5] Pinner, A., and Franz., A., *Ber.*, **38**, 1539 (1905).

[6] Ubber, Dr., *Ch. Zt.*, **28**, 958 (1904).

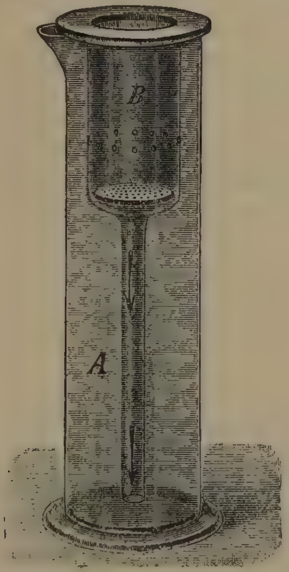

FIG. 131. DISSOLVING AND EXTRACTING WITH COLD SOLVENTS (UBBER)

QUANTITY OF SOLVENTS

The influence exerted on the yield by the quantity of the solvent, even though this be water, is usually not considered. This effect is shown by the increased yield in the following preparation.

Since 1880, glycol has generally been prepared by the convenient method of Grosheintz,[7] that is by boiling ethylene bromide with potash solution, in the proportions of 32 parts of bromide to 250 to potassium carbonate and 350 of water. Although this method is better than all of the previous ones, and has found general favor up to 1897, even it gave very poor yields, and glycol remained a comparatively expensive material. At that time, Hawarth and Perkin[8] overcame this disadvantage. They found that the poor yields of the method were due to the volatility of glycol with steam. They modified the process by having large quantities of ethylene bromide and potassium carbonate react in the presence of relatively small quantities of water. Their procedure followed the previous one in the first stages, *i.e.*, until the ethylene bromide, after long boiling of the mixtures, had disappeared. Fresh quantities of potassium carbonate and ethylene bromide then were added to the liquid containing the glycol. They continued to work in this way for some time. When the mixture contained so much potassium bromide that it crystallized out on cooling, they simply filtered off the salt before adding new quantities of the two reagents. In this way, it was possible to prepare one kilo of glycol in ten to fourteen days, with 1 liter of water, and the yield was 50 to 60 per cent of the theory.

CHOICE AND NATURE OF SOLVENTS AND DILUENTS

In the following, special mention will be made of: Ether, ethylene bromide, alcohol, amyl acetate, benzene, benzoic ester, chloral, carbon tetrachloride, chloroform, dimethyl sulfate, glacial acetic acid, epichlorhydrine, glycerine, methyl ethyl ketone, methylnaphthalene, naphthalene, naphthoic ethyl ester, nitrobenzene, nitromethane, paraffin, *p*-toluidine, phenol, phenyl acetate, pyridine, carbon bisulfide, sulfur dioxide, tricresyl phosphate, toluene, xylene; also sodium chloride, infusorial earth, and sand.

Many of the organic compounds named, which have hitherto been used only as solvents, may also be found useful as crystallizing media.

The value of a suitable solvent may be learned by following the train of thought of Traub, which led him to work out a quantitative procedure for the Tiemann-Reimer synthesis of aromatic aldehydes, twenty years after its publication. In the original form, the yield in many cases is only 5 per cent.

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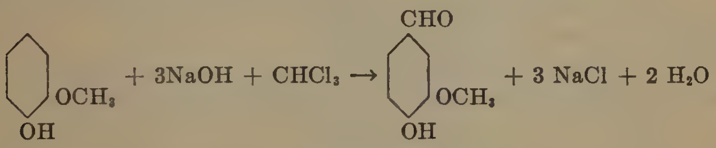
[7] Grosheintz, H., *Bull. soc. chim.*, [2], **31**, 293 (1879).

[8] Hawarth, E., and Perkin, W. H., *J. Ch. Soc.*, **69**, 175 (1896).

Reimer and Tiemann, as well as Koppe and others[9] succeeded in making a large number of aldehydes synthetically, with the aid of this [so-called Tiemann-Reimer] reaction. For this purpose, they boiled a solution of a phenol in ordinary sodium hydroxide of varying concentrations with chloroform for long periods under a reflux. Although this reaction is capable of producing compounds very valuable for technical purposes, it had no technical worth only because of the small yields, the chief product consisting of gummy, dark colored materials.

The discoverers were always perfectly aware of the value of the reaction for possible technical purposes. As early as 1876, in their second communication[10] on this reaction, they stated that they had prepared synthetic vanillin by their new method. This was the first synthesis of this material. The following equation shows the reaction in which methoxyphenol (guaiacol), acts as the phenol.



Somewhat later Traub[11] modified this method so that it could be used on a technical scale. He recognized the reason for the unsatisfactory yield which he remedied in the manner described below. Consequently, the numerous syntheses of vanillin discovered in the meantime, were superseded for practical purposes by this method which was ingeniously developed on the basis of this earliest one.

He found that it was not good to start with a large excess of alkali in the reaction mixture of phenol, chloroform and alkali, since it caused resinification of a considerable part of the aldehyde, because aldehydes in general, under these conditions, are prone to resinify. He combated this by bringing a solution of phenol and chloroform to a boil, under a reflux, with water alone, *i.e.*, without any alkali.

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[9] Reimer, K., *Ber.*, **9**, 423 (1876); Reimer, K., and Tiemann, F., *Ber.*, **9**, 1268 (1876); Tiemann, F., and Koppe, P., *Ber.*, **14**, 2015 (1881).

[10] Reimer, K., *Ber.*, **9**, 424 (1876).

[11] Traub, Max Carl, German patent 80195 (1894); Fr. IV, 1287.

He then slowly added the prescribed quantity of lye to the boiling solution through a dropping funnel. The result of this modification was a considerable improvement; but relatively large quantities of dark, red resins were still formed. Accordingly, the action of the alkali on the aldehydes formed had not been eliminated.

Furthermore, reflection shows that a more rapid reaction could hardly be expected in view of the slight solubility of the chloroform and its considerable stability toward aqueous lyes. A part of the alkali will always be used in the resinification, in so far as the conditions for its reaction with chloroform are not favorable. The formation of worthless by-products is also due, in part, to the relatively high boiling point of the mixture—water solutions of alkalies have a decided tendency to superheat. Consequently, Traub simply used alcohol instead of water as solvent and diluent, and used an alcoholic solution of the alkali.

The success corresponded to the premises. The reaction proceeds much more rapidly; as a rule the resulting solution is hardly yellow, rarely a shade darker, and the product consists almost entirely of aldehydes with no resinous admixtures.

This extraordinarily favorable result may be ascribed to the following circumstances: (1) The use of alcohol, in place of water, as solvent and diluent favors the decomposition of the chloroform, which yields the aldehyde group. It is therefore possible to work more rapidly, and because of the lower boiling point, at a temperature lower than can be used with water. (2) The device of adding the alcoholic alkali to the phenol solution at the same rate as it is used in decomposing the chloroform, largely prevents decomposition by the alkali of the product already formed, or of the phenol which has not yet reacted and may carry sensitive side-groups. (3) The quantity of alkali may now be diminished considerably and the effect of this decrease is in the same favorable direction. (4) The new conditions make it possible to use not only small quantities (formerly[12] not more than 5 grams of guaiacol could be used) but as much as several kilograms may be worked up at one time. As an example, the successful preparation of *m*-methoxy-salicyl aldehyde and of vanillin, from guaiacol, will be given, and will illustrate the technical application of the method as modified by Traub.

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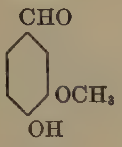
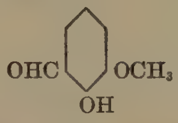
[12] Tiemann, Ferd, and Koppe, Paul, *Ber.*, **14**, 2015 (1881).

Ten kilograms of pure crystalline guaiacol is dissolved in ten times the quantity of 95 per cent alcohol and 50 kgm. of chloroform added. The solution is warmed, almost to boiling, under a reflux. Without further heating an alcoholic solution of 25 kgm. potassium hydroxide or the equivalent quantity of sodium hydroxide is run in through a suitable device. A vigorous reaction begins at once, with separation of chloride, the mixture comes to a boil and stays there until all of the alcoholic lye has run in. After acidifying with hydrochloric or sulfuric acid, the alcohol and the excess chloroform are distilled off to be reused later. Vanillin,



and *m*-methoxy-salicylic aldehyde,



are extracted from the distillation residue, and may then be separated and purified. It can be seen that under the changed conditions of this method of preparing aldehydes, the aldehyde group preferentially enters the phenol in the para rather than the ortho position. In considering the case at hand, since the vanillin is the para compound, this fact is of particular value from a technical standpoint.

Recent communications of Auwers and Keil,[13] which must be mentioned, state that cyclic ketones containing chlorine are also always formed in the preparation of hydroxyaldehydes by the Tiemann-Reimer reaction. The quantity of these formed is determined essentially by the constitution of the phenol used; thus *o*-cresol gives very little, as-*m*-xylenol 30 per cent, pseudo-cumenol 42 per cent, of chlorinated products.

Wohl[14] found that cellulose is easily acetylated by acetyl chloride in the presence of pyridine, while the earlier methods of preparing acetylated cellulose (using acetyl chloride and zinc- or magnesium-acetate,[15] with addition of nitrobenzene) were difficult to use satisfactorily. However, the method became easy to use even in the presence of pyridine only after he added to the mixture a solvent for the cellulose ester formed by the reaction, in order to constantly expose new layers of the insoluble cellulose. Nitrobenzene, acetone, naphthalene, etc., might serve as solvent, and these could be separated later from the cellulose ester by water or alcohol. For instance, 10 kg. of cut paper pulp—the earlier processes were applicable only to the most finely divided cellulose—is moistened with a solution of 20 liters of pyridine in 60 liters of nitrobenzene, and acetyl chloride is run in so slowly that the temperature does not rise above 100°. After digesting for 2 hours, at 80 to 90°, the mass is poured into excess alcohol, and the cellulose ester which constitutes the residue is washed and dried. If 30 liters of benzoyl chloride is used in place of the acetyl chloride, and the digestion continued for two hours, at 150°, a mixture of di- and tribenzoyl cellulose ester results.

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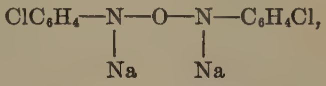
[13] Auwers, K., and Keil, G., *Ber.*, **35**, 4207 (1902).

[14] Wohl, A., German patent 139669 (1899); *Ch. Zt.*, **27**, 285 (1903).

Hofmann[16] had observed that sodium reacts with chlornitro-benzene to form a compound having the formula:



$$\mathrm{ClC_6H_4{-}\underset{\substack{|\\ Na}}{N}{-}O{-}\underset{\substack{|\\ Na}}{N}{-}C_6H_4Cl},$$

but he was not able to obtain the corresponding compound from nitrobenzene in ether solution. Later, Löb[17] found that when sodium is allowed to react on a boiling benzene solution of nitrobenzene, the metal becomes covered with a brown coating which hinders any further reaction, even though the boiling be continued for days. But when he boiled toluene in which sodium melts, and a solution of nitrobenzene in toluene was then slowly run in, the brown sodium compound of nitrobenzene was formed so abundantly when the flask was shaken frequently, that finally the liquid was filled entirely with the compound.

The following example shows the carrying over of an oxidation process, which was generally applicable to aqueous solutions of bases brought into solution by means of acetic acid, to bases which are closely related to the former as to structure, but are insoluble in water, even in the form of their salts. In this case, it has been found possible to use phenol as solvent and diluent, in place of water. However, an oxidizing agent other than that used in the original procedure must be employed. But the oxidation of the bases, which could not be oxidized in the desired manner in aqueous solution, is thus accomplished.

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[15] Cross, C. F., and Bevan, E., German patent 86368 (1895); *Chem. Zeit.*, **20**, 411 (1896).

[16] Hofmann, A. W., and Geyger, A., *Ber.*, **5**, 915 (1872).

[17] Löb, Walther, *Ber.*, **30**, 1573 (1897).

Valuable dyes may be obtained by simultaneous oxidation of equal molar quantities of *p*-aminodialkyl-aniline[18] and *o*-aminodimethyl-*p*-toluidine, with loss of a methyl group from the *o*-aminodimethyl-*p*-toluidine. The reaction is not difficult if the starting materials are soluble in water. For instance, 19 parts α_1, α_2-naphthylenediamine[19] and 15 parts aminodimethyl-*p*-toluidine are oxidized in water solution with 30 parts potassium dichromate and acetic acid, the precipitate filtered off, decomposed by boiling with hydrochloric acid for one hour. The dye is then salted out with sodium chloride. The case is different if one, or both, of the components is slightly or not at all soluble in water, as is true of the salts of tolyl-α_1, α_2-naphthyllenediamine. This difficulty was overcome by using phenol as solvent and pyrolusite as oxidizing agent.

The procedure, in this case, then becomes the following: 7.5 kgm. *o*-amino-dimethyl-*p*-toluidine,[20] 13 kgm. α_1, α_2-naphthylene-diamine, 14 kgm. sodium chloride and 17 kgm. pyrolusite are thoroughly mixed in an enameled kettle provided with a stirrer, and standing in a water bath. Then 25 kgm. phenol is added. The color of the mass changes with further stirring, and finally becomes red. The water bath is now heated and the stirring continued for two hours longer, at 80 to 90°. After the formation of the dye is finished, the phenol and sodium chloride are dissolved in a little warm water, and the crude reaction product is repeatedly extracted by boiling with acidified water, and the dye then salted out of the combined filtrates.

Phenol seems to have so many excellent characteristics as a solvent and diluent that it ought to be used much more frequently.

While very poor yields are obtained from the action of chloral hydrate upon aniline derivatives, these yields become almost quantitative if phenol is used for diluting the anhydride. For instance,[21] if 14 parts of anhydrous chloral are dissolved in 9 parts of phenol, and 12 parts of dimethylaniline run into the solution, after twenty-four hours, very considerable quantities of dimethyl-*p*-amino-phenyl-hydroxy-trichlorethane crystallize out.

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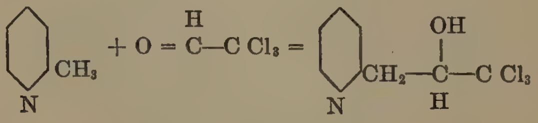
[18] Meister Lucius & Brüning, German patent 69188 (1891); Fr. III, 397.

[19] Meister Lucius & Brüning, German patent 85231 (1892); Fr. IV, 376.

[20] Geigy & Co., German patent 85233 (1895); Fr. IV, 705.

According to statements published in 1905,[22] phenol is the best agent for purifying indigo if the quantity of phenol is so chosen that the impurities alone dissolve, while only a trace of the indigo goes into solution. This procedure for purifying indigo has the advantage over all the methods previously published (see the discussion of pyridine below) since it permits, by a comparatively simple operation, the preparation of almost chemically pure indigo, containing over 99 per cent of the dye. One part of finely ground indigo is thoroughly stirred with 3 parts of crude carbolic acid, and while stirring continuously is heated to 120 to 140°, in an oil bath. After cooling, the contents of the kettle are filtered, washed with carbolic acid, then with dilute sodium hydroxide to remove the phenol, and finally with water. After drying, the indigo content is almost 100 per cent. Cresols, etc., or the ethers of these compounds, naphthyl ether[23] for example, may be used in place of phenol. In this case, the mixture of 1 kgm. of indigo and 3 kgm. of naphthyl ethyl ether is heated to 150 to 160°, filtered after cooling, washed first with the naphthyl ether, then with alcohol and then dried.

According to Einhorn,[24] picoline and chloral react directly upon each other in molecular quantities, forming pyridyl-trichlorhydroxy-propane:



However, so much resinification ensues that the intended further use of this derivative for the preparation of pyridyl-lactic acid would have had to be abandoned, if he had not raised the yield from 100 grams of picoline to at least 125 grams of the hydrochloride of pyridyltrichlorohydroxy-propane, by having present a suitable diluent, in this case amyl acetate. In 175 cc. amyl acetate 50 cc. α-picoline and 45 cc. chloral were dissolved and heated under a reflux for 10 hours in a bath heated to 140 to 150°. When the cooled solution was extracted with dilute hydrochloric acid, the condensation product went into the water layer.

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[21] Bayer & Co., German patent 49844 (1899), Fr. II, 177; Zierold, Georg, German patent 61551 (1890), Fr. III, 109.

[22] Badische A. S. F., German patent 158500 (1903); Fr. VII, 782.

[23] B. A. S. F., French patent 338311 (1903); Fr. VII, 274.

[24] Einhorn, A., *Ann.*, **265**, 210 (1891).

Chloral, *per se,* is a solvent for very many materials. Starches dissolve in it. Very many salts of alkaloids dissolve in chloral diluted with alcohol, and often even the tannates of these compounds. Also the majority of artificial dyes and a great number of natural colors, such as chlorophyll, and the coloring matter of blood are soluble in it.

In this connection it may be mentioned that Beckmann[25] has found ethylene bromide to be well suited for extracting fats from spices because conclusions as to their purity can be drawn from the depression of the freezing point of the ethylene bromide.

Dimethyl sulfate, according to Valenta,[26] has the property of readily dissolving, at ordinary temperatures, hydrocarbons of the benzene series as they are found in coal tar, or of being miscible with them, and therefore, also with coal tar oils in every proportion. On the other hand, it does not dissolve the hydrocarbons with open carbon chains which are found in crude petroleum, and consequently, in the cold it does not dissolve petroleum distillates such as petroleum ether, benzine, polishing oil, coal oil, and light and heavy mineral oils. Resin oils are only very slightly soluble in cold dimethyl sulfate. He has used this behavior of these oils for separating the tar oils from mineral oils, resin oils or mixtures of both to an extent, which for technical purposes, is almost quantitative.

Glycocoll, aminoacetic acid, is prepared by the action of ammonia on either chloracetic acid[27] or on the nitrile[28] of glycollic acid, which is later saponified with alkalies.[29] Both methods yield considerable quantities of glycocoll, but also much ammonium chloride, sodium chloride, etc. Glycocoll is just as soluble in water as are these inorganic salts, and this greatly increases the difficulty of preparing it pure, because the method of Kraut,[30] in which it is recovered as the copper compound is unsatisfactory, at least technically. It was discovered that glycocoll, in contrast to the inorganic salts, dissolves readily in glycerol,[31] even at the temperature of the water bath. Consequently, the reaction mixture containing the glycocoll is brought to dryness and heated to 100 to 150° with glycerine of the highest possible percentage. The inorganic salts soon settle to the bottom and the glycocoll solution is drawn off while still warm. The glycocoll is recovered by distilling off the glycerol in vacuo, or by driving it off with superheated steam. The glycocoll may be precipitated by methyl or ethyl alcohol. In the same way, monomethyl glycocoll (sarcosine) produced by means of methylamine, and the other corresponding homologues, may be obtained pure with the aid of glycerol.

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[25] Beckmann, E., *Ch. Zt.*, **30**, 484 (1906).

[26] Valenta, E., *Ch. Zt.*, **30**, 266 (1906); see Harrison, T. W., and Perkin, F. M., *Analyst*, **33**, 2, (1908).

[27] Hantzsch, A., and Silberrad, O., *Ber.*, **33**, 70 (1900).

[28] Eschweiler, W., *Ann.*, **278**, 237 (1894).

[29] Deutsche Gold- und Silber-Scheide-Anstalt, German patent 169186 (1903); Fr. VIII, 403.

Pyridine also has been used too little, up to the present, as a solvent and diluent. It, also, is said to dissolve easily the brown-red to red by-products present in synthetic indigo that were mentioned above. The finely ground indigo is covered with 5 times its weight of pyridine bases[32] and thoroughly mixed. The mixture is then heated for several hours under a reflux and finally washed on the filter with fresh pyridine until this no longer runs off red.

Glacial acetic acid is used as a solvent exceptionally often. All of the extraction media mentioned, as well as most of the crystallizing media, may also be employed as solvents. Thus, Bischoff[33] added 120 cc. xylene to 90 grams methylmalonic ester and then heated the mixture with 11.5 grams of sodium under a reflux. Brühl[34] used the same diluent after he found that the action of sodium on borneol, diluted with ether or toluene, was unsatisfactory. He[35] also diluted β-methyl-amino-crotonic anilide with benzoic ester when it was to be shaken with sodium hydroxide and benzoyl chloride in order to benzoylate it.

[30] Kraut, K., *Ann.*, **266**, 295 (1891).
[31] Meister Lucius & Brüning, German patent 141976 (1902); Fr. VII, 36.
[32] Meister Lucius & Brüning, German patent 134139 (1901); Fr. VI, 589.
[33] Bischoff, G. A., *Ber.*, **24**, 1046 (1891).
[34] Brühl, J. W., *Ber.*, **24**, 3378 (1891).
[35] Brühl, J. W., *Ber.*, **25**, 1873 (1892).

According to Erdmann,[36] acetylated anthranilido-acetonitrile methyl ester may be separated from any unattacked ester by dissolving it in 10 parts of naphthalene which readily dissolves only the former.

Zetter[37] found that phenanthrene gives different bromine derivatives according to whether the reaction takes place in carbon bisulfide or in ether solution. Pinner[38] was able to obtain perbrominated aldehydes only after diluting the starting materials with acetic ester, while he could not get definite products in the presence of carbon bisulfide or carbon tetrachloride.

Hofmann and Geiger, Martius, as well as Nietzky had unsuccessfully attempted to prepare aminoazo-*p*-toluene from *p*-toluidine dissolved in alcohol, but Nölting and Witt[39] obtained it easily by carrying out the re-arrangement of the diazoamino-*p*-toluene in a solution of fused *p*-toluidine (aniline had previously been used for diazoamino benzene).

According to Beringer,[40] the ketones boiling above 79°, such as methyl ethyl ketone, ethyl butyl ketone, valerone, etc., are much better for extracting coloring matter from plants than are any of the usual solvents, alcohol, ether, acetone, or mixtures such as water and glycerol, etc.

Epichlorhydrin[41] and also phenyl acetate[42] form clear solutions with any desired quantity of gun cotton. Perhaps they could be used for dissolving other nitrates of aliphatic polyatomic alcohols. In 1907 Fischer[43] stated that few general solvents for acetyl celluloses and nitro celluloses were known. Practically, only glacial acetic acid and epichlorhydrin were worthy of consideration but they have various disadvantages. He found that nitromethane

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[36] Erdmann, H., German patent 123695 (1900); Fr. VI, 550.

[37] Zetter, Georg, *Ber.*, **11**, 169 (1878).

[38] Pinner, A., *Ann.*, **179**, 68 (1875).

[39] Nölting, Emilio, and Witt, Otto N., *Ber.*, **17**, 78 (1884).

[40] Beringer, E., German patent 104106 (1898); *Chem. Zentr.*, **70**, II, 923 (1899).

[41] Flemming, H., *Ch. Zt.*, **21**, 97 (1897).

[42] Riddle, R. N., United States patent 797373 (1905); *Chem. Zeit.*, **29**, 962 (1905).

[43] Fischer, E., German patent 201907 (1907); *Chem. Zentr.*, **79**, II, 1398 (1908).

(b.p. 101°) is a general solvent lacking these drawbacks. It is stable and indifferent, has a low boiling point, and is only slightly inflammable, and shows greater solvent powers than the other general solvents. The layers remaining after evaporating the nitromethane from the cellulose acetate and cellulose nitrate solutions, are very hard, transparent, shiny and adhere firmly to glass and other materials.

Weissgerber[44] states that methyl-naphthalene is a solvent in which sodium, for instance, may be allowed to react at 200° on bodies like indole.

It may be stated, with respect to the usefulness of tricresyl phosphate[45] that, when warm, it dissolves solid and liquid hydrocarbons, oils, fats and fatty acids, sulfur, etc., out of materials to be extracted. The dissolved materials may be recovered from the solution thus produced, for instance, by cooling it and mechanically separating the precipitated product (sulfur, paraffin, earth wax) or by distillation under reduced pressure. If vulcanized rubber is digested with tricresyl phosphate, the sulfur dissolves, while the caoutchouc remains behind undissolved, as an elastic mass.

It may be mentioned that toluene[46] is suited for diluting phosphorus oxychloride.

Walden[47] found liquid sulfur dioxide to be an inorganic ionizing solvent of great value. The number of materials that dissolve in this medium, often in unlimited quantities, is very extensive. Another point is, that very many compounds, salts as well as indifferent materials like hydrocarbons, dissolve with characteristic color in liquid sulfur dioxide. Among the readily soluble materials are the inorganic salts, potassium bromide (colorless), potassium iodide, sodium iodide (both with yellow color), sublimed ferric chloride, cobalt thiocyanate; among the organic materials are many hydrocarbons, alcohols, acids, esters, bases, salts, etc. He gives as an example of the metathesis of neutral salts, the interaction of sulfur dioxide solutions of potassium iodide and trimethyl-ammonium chloride, forming insoluble potassium chloride.

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[44] Weissgerber, R., *Ber.*, **43**, 3522 (1911).

[45] Chemische Fabrik von Heyden, German patent 284410 (1913); *Chem. Zentr.*, **86**, II, 55 (1915).

[46] Badische A. S. F., German patent 81264 (1893); Fr. IV, 253.

[47] Walden, P., *Ber.*, **32**, 2862 (1899).

$$\underset{\text{(soluble)}}{KI} + \underset{\text{(soluble)}}{NH(CH_3)_3Cl} = \underset{\text{(precipitate)}}{KCl} + \underset{\text{(soluble)}}{NH(CH_3)_3I}$$

As an instance of the double decomposition between a neutral salt and an acid, bromisobutyric acid dissolved in liquid sulfur dioxide and a solution of potassium iodide, when brought together enter into reaction, and insoluble potassium bromisobutyrate is precipitated:

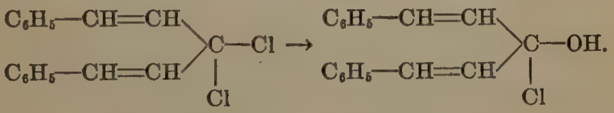
$$KI + (CH_3)_2CBr{—}COOH = \underset{\text{(insoluble)}}{(CH_3)_2CBr{—}COOK} + HI$$

After a long search, Diels[48] found liquid sulfur dioxide to be the solvent in which it is possible to bring about the addition of carbon suboxide to formic acid, since it is indifferent to carbon suboxide and forms a clear solution of formic acid at temperatures about −30 to −40°.

Plauson[49] recommends a solution of gaseous sulfur dioxide in acetone, or a mixture of liquid sulfur dioxide and acetone, as an excellent solvent. It is suitable for extracting coal, lignite, peat, etc.; for the selective extraction of solid or liquid mixtures of hydrocarbons, etc.

The addition of sand, talcum, infusorial earth, sodium chloride,[50] etc., to liquids and solids is an entirely different kind of dilution which is no longer in favor. The infusorial earth often exerts very favorable action as, for example, in sulfonations. This has nothing to do with the dilution, but is a consequence of surface attraction.

Straus and Caspari[51] found that one of the two chlorine atoms is replaced by hydroxyl when moist silver oxide reacts in ether solution upon ketochlorides of the type of dibenzalacetone:



$$\left.\begin{matrix}C_6H_5{—}CH{=}CH\\ C_6H_5{—}CH{=}CH\end{matrix}\right> \underset{\displaystyle Cl}{\overset{}{C}}{—}Cl \rightarrow \left.\begin{matrix}C_6H_5{—}CH{=}CH\\ C_6H_5{—}CH{=}CH\end{matrix}\right> \underset{\displaystyle Cl}{C}{—}OH.$$

To carry out this reaction, they precipitated the silver oxide from 5 grams silver nitrate (calculated for one molecule 3.1 grams) with sodium hydroxide, washed it well by decantation, sucked it dry, and then ground it thoroughly with enough infusorial earth to produce a dry powder. They shook this with a solution of 5 grams dicinnamenyl-dichlor-methane in alcohol-free ether, for about two hours, in a shaking machine, until a filtered test portion no longer formed silver chloride when shaken with fresh silver oxide. The ether solution was dried for a short time with calcium chloride, concentrated on the water bath, and finally evaporated to dryness in a vacuum. The oily residue of dicinnamenyl-chlorcarbinol solidified when rubbed with petroleum ether.

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[48] Diehls, Otto, and Lalin, Leonid, *Ber.*, **41**, 3426 (1908).

[49] Plauson, H., *Ch. Zt.*, **46**, 555 (1922).

[50] Banse, G., *Ber.*, **27**, 2165 (1894).

[51] Straus, F., and Caspari, F., *Ber.*, **40**, 2698 (1907).

Heusler[52] states that after he had learned how to decompose aromatic diazo-amino compounds without danger of an explosion, by diluting them with sand, he later found liquid paraffin to be far more convenient. For instance, if diazoaminobenzene, or its homologues, is covered with 8 to 10 times its weight of this material, the diazoamino compound dissolves on warming, and a perfectly quiet evolution of nitrogen occurs on further heating.

Finally, it may be mentioned that many solids, when brought together, mutually liquefy each other, even in the absence of any solvent. For instance, as Brown first observed, if equal parts of chloral hydrate and camphor or menthol are rubbed together, a viscous liquid which will no longer solidify, is obtained.[53] Likewise, Wallach[54] states that two isomeric oximes prepared by him, when rubbed together, soon liquefied and remained for months as an oil, although each one alone, crystallized well. According to Vorländer,[55] crystalline liquid mixtures in which the mutual relative quantities may vary widely, are obtained by grinding anisic acid with anisal-propionic acid.

SOLUTIONS OF INORGANIC AND ORGANIC ALKALI SALTS AS SOLVENTS

Solutions of the following materials will be discussed: Alum, anisole sulfonic acid, borax, urea, sodium chloride, sodium cresotinate, sodium naphthylsulfinate, sodium bisulfite, potassium oleate (soaps); potassium phenyl-xylyl-ethane sulfonate, sodium salicylate, and sodium toluene sulfonate.

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[52] Heusler, Fr., *Ann.*, **260**, 228 (1890).

[53] Schär, E., *Arch. Pharm.*, **233**, 6 (1895).

[54] Wallach, O., *Ann.*, **262**, 340 (1891).

[55] Vorländer, D., *Ber.*, **40**, 1970 (1907).

In the dye industry, it has long been known that certain organic dyes which dissolve little, if at all, in pure water, dissolve in salt solutions. Thus purpurin (trihydroxyanthraquinone) dissolves in boiling alum solution, which, in fact, also dissolves the alumina compound of this dye (that is, its lake which is insoluble in water). The solubility of purpurin in such solutions is used, according to recent patents, to remove it from mixtures of dyes, if the admixed dyes do not show this solubility. Further, Schunck and Roemer[56] state that purpurin can hardly be separated from alizarin except by repeated crystallizations from hot alum solution, which scarcely dissolves alizarin.

Cold saturated borax solution dissolves many dyes which otherwise do not dissolve in water. For instance, if sandal wood has been boiled with water to extract the tannic acid from it, borax solution will later completely remove the coloring matter, santalin. It may then be precipitated from this solution by sulfuric acid. These details were investigated by Palm.[57]

Link[58] was the first to use soap solutions for dissolving tar oils, because as early as 1885, he proposed purifying crude naphthalene by stirring it for some time at 85° with soap solution which dissolves the greater part of the mass. The solution is cooled in large vessels to 50°, by the addition of water; the deposit is centrifuged and distilled. Practically pure naphthalene passes over and later solidifies as a snow-white mass.

A potassium soap well suited for disintegrating materials insoluble in water may be prepared, according to Beysen,[59] by shaking together 500 parts melted cocoanut oil, 330 parts potash lye of 40° Bé, 200 parts of spirit. Saponification soon begins with evolution of heat. The jelly-like soap formed is neutralized with oleic acid, and then diluted to 2000 parts with distilled water, forming an approximately 50 per cent potassium liquid soap which takes up creosote, paraform, etc., very well. A French patent[60] gives details as to the use of potassium oleate as an excellent aqueous solvent for basic aniline dyes. According to it, for instance, a rapid drying copying ink may be made by heating 6 parts of benzyl violet base, 20 parts oleic acid, 100 parts printer's ink and 4 parts potash lye (d. 1.36).

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[56] Schunck, E., and Roemer, H., *Ber.*, **10**, 551 (1877).

[57] Palm, R., *Z. analyt. Ch.*, **22**, 324 (1883).

[58] Link, G., German patent 35168 (1885); Fr. I, 11.

[59] Beysen, *Apoth. Zt.*, **19**, 189 (1904); *Ch. Zt. Rep.*, **28**, 80, (1904).

[60] B. A. S. F., French patent 338857 (1903); *Ch. Zt.*, **28**, 873 (1904); German patent 172465 (1903); Fr. VIII, 838.

It is of practical importance that, after Fraenkel[61] had verified the high disinfecting value of the coal tar cresols, which were supposed to be insoluble in water, it was found that these cresols are soluble in strongly alkaline soap solutions. This led to the preparation of Lysol,[62] Creolin, Sapocarbol, etc.

The disadvantage of the strong alkalinity of soap solutions was later overcome when it was found that the cresols could be brought into a neutral aqueous solution by means of sodium salicylate[63] or, still better, by sodium cresotinate. Solveol[64] is a solution of cresols in sodium cresotinate; Solutol,[65] a solution of cresol in the sodium salt of cresol. The aqueous solutions of the alkali salts of phenyl-xylyl-ethane sulfonic acid[66] and hydrindene sulfonic acid[67] are claimed to have the property of dissolving tar oils as well as the cresols and their homologues, to a great degree.

Acids, alkalies, alcohol, glycerol, etc., are ordinarily added to stabilize aqueous solutions of coal tar dyes, (such as metanil yellow, rhodamine, etc.,) which are difficultly soluble in water or which separate from solution at lower temperatures. The action of these is limited, furthermore the solution is not neutral, and sometimes the shade is altered considerably. Nottbrack[68] prepared neutral, stable, aqueous solutions of such dyes without change of shade, by adding 5 to 20 per cent or even more, of turkey red oil. For instance, 20 grams of 70 per cent turkey red oil was mixed with 80 grams water and enough caustic potash lye added to form a perfectly clear neutral liquid. This mixture dissolves, even in the cold, dyes which otherwise require heating to be brought into solution. It is possible, in this way, to prepare clear, neutral and stable solutions of dyes, such as metanil yellow and rhodamine which mutually precipitate each other. Each dye is dissolved separately and the solutions united. This produces a perfectly clear mixed dye solution which is neutral and of the desired shade. The quantity of turkey red oil to be added to the solution is determined by the dye, and by the concentration desired. Turkey red oil also dissolves hydrocarbons, carbon tetrachloride, etc., and such aqueous solutions dissolve fats from fabrics,[69] for example, and in this way, the unfavorable action of the soaps customarily used is avoided.

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[61] Henle, A., and Fraenkel, C., *Z. f. Hygiene*, **6**, 521 (1889); *Arch. Hygiene*, **9**, 188 (1889).

[62] Raupenstrauch, G. A., *Arch. Pharm.*, **229**, 197 (1891).

[63] von Heyden, F., German patent 57842 (1890); *Ber.*, **25** R, 184 (1892).

[64] Hiller, A., *Deutsche med. Wochenschrift*, **18**, 841 (1892); Engler, C., and Dieckhoff, E., *Archiv. d. Pharm.*, **230**, 561 (1892); *Archiv. d. Pharm.*, **232**, 351 (1894).

[65] *Pharmaceut. Centralhalle*, **33**, 304 (1892).

[66] Ch. Fab-A-G. in Hamburg, German patent 72101 (1892), Fr. III, 986; Ritsert Eduard, German patent 147790 (1902), Fr. VII, 639.

[67] Kraus, A., *Arb. Kaiserl. Gesundheitsamt*, **26**, 130 (1907); see also A. G. für Teer u. Erdölindustrie, German patent 128800 (1901); *Ch. Zt.*, **26**, 207 (1902).

[68] Nottbrack, Friedrich, *Ch. Zt.*, **32**, 100 (1908).

Formerly, *o*-nitrophenyl-lactic acid-ketone had been dissolved only in acetic acid, but this material may also be dissolved easily in the following way; a fact of great value to the indigo dyers, for some time. One kilogram of ketone[70] is mixed with 3 kgm. sodium *p*-toluene-sulfonate or *m*-xylene sulfonate, and a stable product is obtained that is soluble in 10 parts of water.

The amino-carboxylic esters combine with the sulfonic acids of the phenol ethers to form water soluble compounds, just as they do with the phenol sulfonic acids. Thus, the compound of anisol-sulfonic acid with *p*-aminobenzoic ethyl ester.[71]

$$CH_3O \cdot C_6H_4 \cdot SO_3H \cdot H_2N \cdot C_6H_4 \cdot CO_2C_2H_5$$

may be prepared by heating equivalent quantities of anisole and sulfuric acid on the water bath for two hours; diluting the sulfonation mixture with an equal weight of water, and then adding one-fourth of its weight of *p*-aminobenzoic ester to the warm solution. At first, everything dissolves, but the new compound soon crystallizes out.

It may be mentioned that phenylhydrazine is insoluble in water, but soluble in salt solutions. Thus, Otto[72] states that if phenylhydrazine is added to a solution containing enough alkali salt of naphthyl sulfinic acid, it will dissolve immediately on shaking, producing a liquid which is miscible with phenylhydrazine in every proportion. Phenylhydrazine suspended in water, may be easily extracted with ether, but it is very difficult to remove it by means of ether from the above liquid from which phenylhydrazine cannot be precipitated by the addition of water. Phenylhydrazine shows the same behavior toward soap solutions and toward solutions of sodium salicylate. Such solutions of phenylhydrazine may perhaps be used when it is not desired to use the customary alcoholic or ether solutions of this base.

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[69] Krüger, Gerh., *Ch. Zt.*, **32**, 935 (1908).

[70] Soc. Chim. des Usines du Rhône, German patent 148943 (1902), Fr. VII, 275; see also German patent 160783, Fr. VIII, 423.

[71] Ritsert, Eduard, German patent 149345 (1902); Fr. VII, 641.

[72] Otto, Robert, *Ber.*, **27**, 2131 (1894).

Many albuminous materials, both of animal and vegetable origin, are not soluble in pure water, but may be dissolved in brine or similar salt solutions. Recent experiments have shown that sodium bisulfite solutions are particularly useful because they very freely extract albumins, especially from vegetable raw material. May it perhaps not be that the aldehyde groups, assumed to be present in the albumins, combine with the bisulfite and thus produce water soluble compounds of it and albumin?

If the remarkable solvent power of urine for materials of all kinds, which can only be due to the presence of urea, is recalled, solutions of urea may be expected to dissolve many materials.

In conclusion, it may be pointed out that these relations are found to hold for not only organic and natural bodies, but that similar observations have been made in the inorganic field. For instance, lead sulfate insoluble in water, dissolves freely in sodium acetate solution.

ORGANIC SOLVENTS AND INORGANIC MATERIALS

The following solvents are discussed: Acetone, ether, ethyl alcohol (and the different behavior of methyl alcohol), allyl alcohol, amyl alcohol, aniline, benzene, acetic ester, methyl acetate, methyl alcohol, pyridine.

Solutions of inorganic compounds are often allowed to act on organic liquids, especially alcoholic solutions. In dealing with inorganic salts, it is best to choose, if possible, salts soluble in alcohol, since their aqueous solutions usually give poor yields. Thus sodium bromide or iodide, which are easily soluble in alcohol, may be used in place of potassium bromide or iodide. An excellent substitute for potassium sulfocyanate is the barium salt which is very soluble in alcohol. This was first recommended by Tscherniac.[73] Copper chloride, lead chloride and lead acetate, for example, dissolve readily in alcohol. Gabriel[74] purified ethyl mercapto-phthalimide by adding to its hot alcoholic solution a hot alcoholic solution of sugar of lead clarified with a little acetic acid. The insoluble mercaptan lead compound precipitated at once. No cyanide corresponding to the above salts, to replace potassium cyanide, appears to be known. Perhaps occasionally, calcium cyanide and ammonium cyanide could be used to advantage. A solution of calcium cyanide may be obtained, according to Franzen,[75] by dissolving 33 grams potassium cyanide in 100 cc. water and mixing it with a solution of 28 grams anhydrous calcium chloride in 100 cc. water, and filtering off any calcium carbonate that may have precipitated. It is, for instance, a general reagent for aldehydes and ketones; thus it combines with benzaldehyde when shaken with it, and forms the calcium compound of mandelic nitrile:

$$2\ C_6H_5\cdot CHO + Ca(CN)_2 = [C_6H_5\cdot CH(CN)O]_2Ca$$

Lubawin[76] has shown that the cyanide of α-aminobutyric acid is formed by allowing an aqueous solution of ammonium cyanide to stand for some time with acetone:

$$(CH_3)_2CO + NH_4CN = (CH_3)_2\ C(CN)NH_2 + H_2O$$

Zelinsky and Stadnikoff[77] later showed that equal molecular quantities of dissolved potassium cyanide and ammonium chloride exert the same action, and its general application has made accessible a large number of α-amino acids.

Table 6, solubility table, was compiled by Lobry de Bruyn.[78] It gives the solubility at room temperature.

According to Naumann,[79] pyridine and especially methyl acetate dissolve; potassium sulfocyanate, iodide,* permanganate; sodium iodide, sulfocyanate; lithium bromide, chloride,* iodide, sulfocyanate; rubidium iodide; ammonium sulfocyanate; barium iodide, bromide;* strontium bromide; calcium nitrate, bromide; magnesium bromide,* iodide;* cuprous bromide,* chloride,* iodide; cupric bromide, chloride, sulfocyanate; zinc bromide, chloride, iodide, nitrate; lead iodide;* cadmium bromide,* iodide; cerium chloride,* bromide; chromic chloride,* acid anhydride; manganous chloride;* ferric chloride; ferrous chloride;* cobalt bromide, chloride, iodide, nitrate sulfocyanate; nickel chloride,* nitrate;* thallium chloride,* iodide;* uranium bromide, nitrate; uranyl chloride, iodide; bismuth chloride, iodide; stannous chloride; stannic iodide; silver nitrate,* arsenite; mercuric chloride, bromide, iodide, cyanide, potassium iodide; mercurous iodide, nitrate; gold bromide; platinum chloride;* palladious iodide; iodine; sulfur.* The materials marked * are difficultly soluble.

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[73] Tscherniac, J., and Hellon, R., *Ber.*, **16**, 348 (1883).

[74] Gabriel, S., *Ber.*, **24**, 1112 (1891).

[75] Franzen, Hartwig, *Ber.*, **42**, 3293 (1909).

[76] Lubawin, N., *J. Russ. Phys.-chem. Soc.*, **13**, 504 (1881); Gulewitsch, W., *Ber.*, **33**, 1900 (1900); Bucherer, H., and Grolée, A., *Ber.*, **39**, 1224 (1906); Ch. Fabr. Hofmann & Schoetensack, German patent 85230 (1895), Fr. IV, 160.

[77] Zelinsky, N., and Stadnikoff, G., *Ber.*, **39**, 1724 (1906).

[78] Lobry de Bruyn, C. A., *Z. ph. Ch.*, **10**, 783 (1892).

[79] Naumann, Alex., *Ber.*, **37**, 4609 (1904); *Ber.*, **42**, 3789 (1909).

TABLE 6

Solubility table compiled by Lobry de Bruyn

COMPOUND	METHYL ALCOHOL	ETHYL ALCOHOL
	per cent	*per cent*
NH_4Cl	3.35	0.62
NaBr	17.0	—
KBr	1.51	0.13
NaI	77.7	43.1
KI	16.5	1.75
NH_4NO_3	17.1	3.8
$AgNO_3$	3.72	3.1
$NaNO_2$	4.42	0.31
KCN	4.91	0.87
$NH_2OH \cdot HCl$	16.4	4.43
$BaBr_2$	61.0	2.8
$CuCl_2$	68.0	52.9
$HgCl_2$	66.9	49.5
$Hg(CN)_2$	44.2	10.1
NH_3 at 0°	41.5	24.5
NH_3 at 28°	17.4	10.1
SO_2 at 0°	247.0	115.0
SO_2 at 26°	47.0	32.2
HCl at 0°	105.0	83.0
HCl at 32°	75.1	61.6

According to Holm,[80] 100 grams glycerol at 20° will dissolve the materials shown in table 7.

Ninety per cent alcohol dissolves 0.054 per cent potassium carbonate; 0.038 per cent sodium carbonate.

Laszczynski[81] particularly, has published data as to the solubility of many inorganic salts in organic solvents at the boiling point. Boiling acetone dissolves 1.21 per cent potassium iodide, 20.4 per cent potassium sulfocyanate, over 100 per cent mercuric chloride, 6.07 per cent mercuric iodide, 0.35 per cent silver nitrate. He does not state that it also dissolves potassium permanganate, forming a solution often used for oxidations. As early as 1858, St. Gilles[82] pointed out that acetone dissolves this salt without reacting with it. In 1901 Sachs,[83] supplementing this forgotten observation, stated that acetone dissolves about 2.4 per cent of permanganate at 20°, and about 4 per cent at 40°.

TABLE 7

Materials soluble in glycerol

	GLYCEROL, d. 1.2326, 88 PER CENT	GLYCEROL, d. 1.2645, 100 PER CENT
Lead acetate	129.3	143.0
Sodium borate	89.36	111.15
Potassium bromide	20.59	17.15
Potassium chlorate	1.32	1.03
Potassium iodide	58.27	50.70
Boric acid	13.79	24.80

Ether dissolves 6.38 per cent mercuric chloride, 0.97 per cent mercuric iodide, 11.38 per cent stannous chloride ($SnCl_2 \cdot 2H_2O$). Amyl alcohol dissolves 9.5 per cent mercuric chloride, 3.15 per cent potassium sulfocyanate.

Aniline dissolves 1.1 per cent lead iodide.

Benzene dissolves 1.80 per cent mercuric chloride, 1.24 per cent mercuric iodide. Ethyl acetate dissolves 35.89 per cent mercuric chloride, 4.31 per cent mercuric iodide. Pyridine dissolves 3.2 per cent potassium sulfocyanate, 14 per cent lithium chloride, 8.6 per cent silver iodide. Sachs states that boiling pyridine also dissolves potassium permanganate, and this is not reduced, even after long heating at the boiling point.

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[80] Holm, K., *Pharm. Weekbl.*, **58**, 860, 1033 (1921).

[81] Laszczynski, St. von, *Ber.*, **27**, 2286 (1894).

[82] St. Gilles, Pean de, *Ann. ch. ph.* [3], **55**, 396 (1859).

[83] Sachs, Franz, *Ber.*, **34**, 497 (1901).

While preparing allyl cyanide from allyl iodide and potassium cyanide, Rinne[84] observed that if ethyl alcohol were used as diluent, a compound of allyl cyanide and alcohol, $C_3H_5CN+C_2H_5OH$, was formed, which boiled at 173 to 174°. When he used allyl alcohol, $C_3H_5CN+3C_3H_6O$ resulted; a fact which has remained unique.

In many cases, it is possible to replace the inorganic salt of an acid by one of its esters which decomposes readily. This has been found to be of value, for instance, in the preparation of diazo compounds of the aliphatic series, by means of amyl nitrite in alcoholic solution. With the exception of this case, the field has hardly been touched, but attempts should be made to use this method to obtain compounds whose preparation is now difficult.[85]

In the chapter on crystallization, it was stated that methyl alcohol in general, lies between water and ordinary alcohol as a crystallizing medium. Consequently, methyl alcohol is usually a much better solvent for inorganic salts than ethyl alcohol. The data of Lobry de Bruyn[86] concerning methyl alcohol will now be continued. The solubility of sodium, or more exactly, of sodium methylate in methyl alcohol is considerably greater than that of sodium ethylate in ethyl alcohol. It is easy to obtain solutions containing 0.1 to 0.125 gram sodium per cc. methyl alcohol. The methyl alcoholic solutions, even when very concentrated, have the great advantage over the ethyl alcoholic ones in that they do not become brown in contact with the air. However, all contact with organic materials, cork for instance, must be avoided while they are being prepared. When adding the sodium, the methyl alcohol must be cooled at first, but heated later. Such solutions remain unchanged and their strength unaltered, after six months.

From the differing behavior toward the oxygen of the air, of the two concentrated alcoholate solutions, it follows that sodium ethylate is more readily oxidized (its alcohol content goes over to aldehyde more easily) that is, it has a stronger reducing action than sodium methylate and this is of interest when reducing nitro compounds.

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[84] Rinne, A., *Ber.*, **6**, 389 (1873).

[85] Ethyl nitrite, readily generated as a gas by dropping dilute sulfuric acid into a mixture of alcohol and dilute sodium nitrite, is in some cases even superior to iso-amyl nitrite, in that no higher alcohol is present in the reaction mixture.—H. T. C.

[86] Lobry de Bruyn, C. A., *Ber.*, **26**, 268 (1893).

When chlorine was passed into ethyl alcohol, it reacted vigorously, since 50 cc. rose to the boiling point in nine minutes, while the temperature of the same volume of methyl alcohol only rose 8° in twelve minutes. Methyl alcohol dissolves 27 per cent chlorine at 0° and 42 per cent at −11.5°.

If 0.5 to 1 cc. bromine is added to 10 cc. alcohol, much heat is evolved and the odor of aldehyde is very marked. No reaction with methyl alcohol can be observed under like conditions. Even larger quantities of bromine may be poured into methyl alcohol, provided it is kept cool. A mixture which initially contained 61.7 per cent bromine still contained 57 per cent after seventy-eight days.

Both alcohols dissolve rather large quantities of iodine. It slowly reacts with ethyl alcohol, but there is no measurable effect on methyl alcohol.

Methyl alcohol is somewhat more hygroscopic than ethyl alcohol; 150 cc. methyl alcohol, after standing for twenty-four hours in the air, had evaporated to 73 cc. and had absorbed 4.5 grams water, while under the same conditions, of 150 cc. ethyl alcohol, 105 cc. containing 3.4 grams water remained.

Since methyl alcohol also dissolves hydroxylamine hydrochloride, Bamberger and Renaud[87] produced a solution of free hydroxylamine, in the following way: They dissolved 3.55 grams of well dried hydroxylamine hydrochloride in a little methyl alcohol and added, while cooling with ice, a concentrated methyl alcoholic solution of sodium methylate prepared from 3.7 grams of the metal.

Forcrand[88] states that ethyl alcohol does not react with copper sulfate. Methyl alcohol, on the other hand, forms the compound $CuSO_4+2CH_3OH$. Barium oxide is readily dissolved by absolute methyl alcohol but is taken up very slowly by absolute ethyl alcohol, and is precipitated from the latter solution only by the addition of water.

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[87] Bamberger, E., and Renauld, E., *Ber.*, **28**, 1683 (1895); Lobry de Bruyn, C. A., *Rec. trav. chim.*, **10**, 102, (1891).

[88] de Forcrand, R., *C. r.*, **102**, 551 (1886).

CHAPTER XIV

MOLECULAR WEIGHT DETERMINATIONS

Molecular weights are determined at present: (a) from the density of the material in the gaseous state (often known as determination of vapor density); (b) from the depression of the freezing point; (c) from the elevation of the boiling point; (d) by comparing the vapor pressures of two solutions in a capillary under the microscope.

Of the many procedures for determining the vapor pressure, which have been proposed from time to time, only the method of air replacement, proposed by Victor Meyer, will be given. It has never been excelled, is very convenient, and consequently, it alone continues to be used.

BASES OF THE METHODS A, B, C

(a) The vapor density methods rest upon the Boyle-Mariotte law which states that all gases behave alike when subjected to changes of pressure and temperature. This is only explicable if equal volumes of all gases under the same temperature and pressure contain the same number of molecules. Consequently, the molecular weight of any substance that can be gasified without decomposition, may be found by comparing the density of its vapor with that of hydrogen whose weight is taken as unity. Although the density of hydrogen is taken as 1, its molecular weight is 2, since the molecule of hydrogen consists of 2 atoms, and consequently when computing molecular weights, the specific gravities of gases compared with hydrogen, must be multiplied by 2. The specific gravities of gases, permanent at ordinary temperature, are easily obtained by direct weighing. These figures multiplied by 2, give the molecular weights. However, there are no balances capable of weighing directly hot vessels filled with the vapors of the substance in question, and so this weighing must be accomplished in some other manner for all materials which are not gaseous at ordinary temperature, but which may be vaporized without decomposition by heating. All of the methods proposed for the determination of vapor density serve this purpose, since it is possible with any of them, to determine the specific gravity of substances in the gaseous condition, where vapors cannot be weighed directly.

(b) and (c) The possibility of determining molecular weights by depression of the freezing point, or elevation of the boiling point, is based on "osmotic pressure." The molecules of a dissolved substance have a tendency to distribute themselves uniformly throughout the solvent, just as gases diffuse uniformly throughout the space in which they are confined. Consequently, the size of the molecules plays no part with respect to osmotic pressure, but their number alone is of moment.

The freezing point method is based particularly upon the following considerations: (1) Solutions freeze at a lower temperature than does the solvent itself; (2) The depression of the freezing point due to the solute corresponds exactly to the concentration of the solution; (3) The freezing point of a solvent is depressed by a certain number of dissolved molecules to the same degree, no matter what the nature of these molecules, *i.e.*, it makes no difference what material is dissolved. It seems hardly necessary to emphasize that this solution may not involve any chemical action of the substances upon each other.

The boiling point method is based upon the same principles, properly applied, which were just enumerated for the freezing point method: (1) Solutions boil at temperatures above the boiling point of the solvent; (2) The elevation of boiling point due to the dissolved material, corresponds exactly to the concentration of the solution. (3) The boiling point of the solvent is raised to the same degree by a definite number of dissolved molecules, entirely independent of their nature.

METHOD OF DETERMINING DENSITY OF GASES BY DISPLACEMENT OF AIR

According to Victor Meyer

If a vessel[1] of the form shown in figure 132, with a capacity of approximately 100 cc., and closed by a rubber stopper always inserted to the same depth, (which in later models is replaced by a cock) is immersed in the vapor of a boiling liquid, or if very high temperatures are to be used, is plunged in a metal bath, the temperature will become constant after heating for some time. No more air will then escape from the exit tube, *a*, at *f*, and this may easily be recognized by the fact that no more bubbles rise from the opening *f*, which is under water in a trough. A graduated tube filled with water is then slipped over *f*, the cock *d* opened, a weighed sample of the substance introduced, and *d* quickly closed. If the temperature is high enough, the sample vaporizes and a volume of air equal to the volume of the vapor flows out of *f*, and may be measured in the calibrated tube. The bottom of the air chamber is covered with some sand or asbestos so that it will not be broken by the falling sample tube. If the quantity of substance is so small that the vapor only fills the lower part of the vessel, and if the vaporization is very rapid, the error arising from the diffusion of the vapor, will be very small

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[1] Meyer, Victor, *Ber.*, **11**, 1867 (1878).

The special apparatus[2] has the following form. The gas delivery tube *a*, is made as narrow as possible. It is 1 mm. in diameter and 140 mm. long. The quantity of substance is chosen so that its vapor occupies less than half the capacity of the glass apparatus *b*. The latter consists of a cylindrical vessel of about 100 cc. capacity, 200 mm. high. To it is fused a glass tube 600 mm. long and 4 to 6 mm. internal diameter. The narrow delivery tube, *a*, is sealed in at a height of 500 mm. When working at temperatures up to the boiling point of diphenylamine (310°) the vessel is suspended in a glass flask whost bulb holds about 80 cc., and whose neck is about 520 mm. long and 40 mm. wide. The following heating liquids may be used: water; toluene (111°); xylene (140°); aniline (183°); ethyl benzoate (213°); amyl benzoate (262°); α-naphthylamine (300°) and diphenylamine (310°). These materials need not be pure, since even mixtures attain constant boiling points when boiled under a reflux, and the boiling point does not enter into the calculation.

For temperatures above 310°, iron tubes welded together at the bottom (gas pipes) should be used as vapor jackets.[3] They should be charged once for all with anthracene (335°), anthraquinone (368°), or sulfur (440°) and held in readiness. For still higher temperatures (518°), and iron tube charged with phosphorus pentasulfide[4] may be used. Since this is not stable in the air, it is well to prepare it freshly by melting together red phosphorus and sulfur in the proportion of 2:5 parts by weight. The crude product may be employed.

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[2] Meyer, Victor, and Meyer, Carl, *Ber.*, **11**, 2254 (1878).

[3] Meyer, V., *Ber.* **17**, 1335 (1884); see also Mai, J., *Ber.*, **41**, 3897 (1908).

[4] Hittorf, J. W., *Pogg, Ann.*, **126**, 193 (1865). The use of phosphorus pentasulphide for vapor density determinations was originated by Hittorf.

A bath of molten lead[5] will serve for still higher temperatures, but is seldom necessary for organic materials.

The determination of vapor density is begun by placing the vessel *b* whose capacity need not be known, in the vapor jacket. As mentioned above, the bottom of this vessel has been covered with asbestos, sand or even mercury. The delivery tube *a* opens under water in a trough. The upper opening of the glass apparatus *b* is closed by a Mahlmann dropping device[6] which consists of a glass cock with a very wide passage through which the sample tube (see below) passes easily. This cock is sealed in the upper part of the neck of the apparatus, several centimeters below the stopper. After the temperature has become constant, the weighed sample is introduced into the small space between the cock and the stopper, and by opening the cock it is allowed to fall into the vessel. A graduated tube, like those used for nitrogen determinations, is filled with water, and is held in readiness in the trough and is then slipped over the mouth of the delivery tube. The sample vaporizes in about one-fourth of a minute and rapidly forces into the tube a volume of air equal to that of the vapor. As soon as no more air bubbles escape, the stopper is removed and the measuring tube is placed in a large cylinder filled with water, so that the level within and without the tube is the same. After some time, the volume of air is read off, and the height of the barometer and the temperature of the water in the cylinder noted, and sufficient data to calculate the density by means of the formula:

$$D = S\,\frac{(1 + 0.003665\,t) \cdot 587780}{(B - w) \cdot V}$$

are then at hand. The symbols in the formula have the following significance:

S = the weight of substance used;
B = the barometer reading reduced to 0°;
w = tension of water vapor at temperature t,
V = measured volume of air;
t = temperature of the room or of the water in the cylinder.

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[5] Meyer, Victor, and Meyer, Carl, *Ber.*, **11**, 2255 (1878).

[6] Meyer, V., and Pond, G., *Ber.*, **18**, 1624 (1885).

The sample is weighed in small weighing bottles; solids are formed into rods which are allowed to fall, without a container, into the apparatus. These may be prepared very easily from fusible materials as follows:[7] The material is melted in a small dish and the fused mass is drawn up into a glass tube about 2 mm. wide and 6 cm. long, until the tube is two-thirds full. The liquid mass usually solidifies very rapidly in the cold glass tube, and when thoroughly solid, it adheres to the glass at only a few points. If the tube is moved to and fro over a small flame so that the substance just begins to melt at the places where it touches the glass, the whole mass may be easily pushed out of the tube by means of a wire as a rod of uniform thickness. V. Meyer recommends the general use of these rods because of the great convenience of storing them, and of introducing them into the vapor density apparatus. A maximum of 0.1 gram substance should be taken, so that its vapor will certainly not occupy more than 50 cc.

When working with materials which react with oxygen, the vessel *b* is previously filled with dry nitrogen in place of the air. This is led in through a glass tube extending to the bottom of the vessel, until all of the air is expelled, or vessels which have a tube sealed[8] to them, as shown in figure 132 may be used. These permit the introduction of nitrogen from below. Very pure nitrogen in large quantities is best prepared, according to Berthelot and Recoura,[9] by absorbing the oxygen from the air, first by metallic copper and ammonia, and completing the removal by cuprous chloride. Such nitrogen is in no way affected by electric sparking.

DETERMINATION OF MOLECULAR WEIGHTS BY THE FREEZING POINT AND BOILING POINT METHODS

Thermometers

Thermometers devised by Beckmann for this purpose are usually employed. They may be used for any temperature encountered in these determinations. They have a range of only about 5 to 6 degrees, which are divided into hundredths. Since each degree covers about 4 cm. it is possible, with the aid of a magnifying glass,[10] to read hundredths of a degree directly, and to estimate the thousandths

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[7] Demuth, R., and Meyer, V., *Ber.*, **23**, 313 (1890).

[8] Grünewald, W., and Meyer, Victor, *Ber.*, **21**, 688 (1888).

[9] Berthelot, M., *Bull. soc. chim.* [2], **13**, 314 (1870); *Bull. soc. chim.* [3], **2**, 643 (1889); see also Threfall, R., *Ber.*, **26** R, 173 (1893).

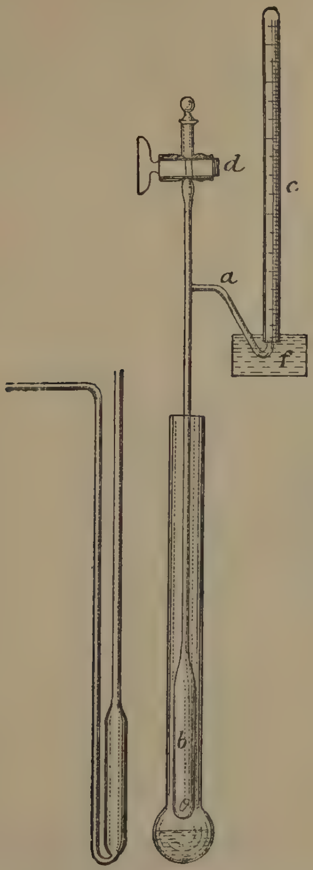

Fig. 132. Apparatus for the Determination of Vapor Density (Victor Meyer)

with certainty (fig. 133). This is possible because a pear shaped reservoir is fused on above over the capillary and this contains any excess mercury as may be seen in figure 134. The reserve of mercury in the extension can be united with, or separated from, the mercury thread of the capillary at will. If the temperature to be read is t, and if that portion of the capillary extending from the end of the scale to the pear shaped reservoir is t' degrees on the scale, and if the thermometer is to be set at the point t'', and if a is the highest point of the scale, the thermometer is warmed in a suitable environment to $[t + t' + (a - t'')]$, and the mercury issuing into the reservoir is broken off by tapping.

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[10] Zeller, Ludwig, H., *Ch. Zt.*, **31**, 115 (1907).

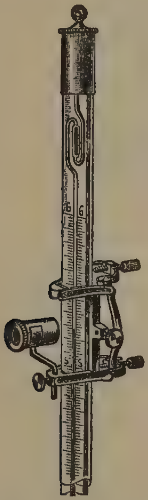

Fig. 133. Reading Thermometer with Magnifying Glass

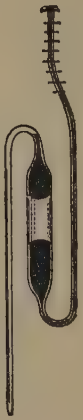

Fig. 134. The Pear-Shaped Reservoir of the Thermometer

When determining freezing points in glacial acetic acid, enough mercury must be removed from the capillary, so that readings may be made at 16° or lower. This is done by immersing the thermometer in water at 17 to 18°, and the mercury leaving the capillary is forced down into the bend of the reservoir by a quick downward jerk. When the instrument is cool it is possible to read the temperature on the scale, but if not, the operation is repeated. If too much mercury was removed this is easily remedied by lightly tapping the side of the reservoir, thus spraying droplets of mercury near the capillary and enough of these are united with the mercury thread, by warming until the column, when cool, is of the proper length. All of the mercury reserve may be united easily by inverting the thermometer, allowing some mercury to enter the reservoir, and then lightly jerking downward. The arrangement makes it impossible for the detached mercury to fall back, nor is mercury ever torn from the capillary when it has partially entered the reservoir while the thermometer is in use. Any difficultly soluble materials may be dissolved by stirring and by heating to higher temperatures, without regard for the thermometer and without removing it.

In order to keep the thermometer permanently free from irregularities at temperatures of 100° or over, it is necessary, according to the later publications of Beckmann,[11] to remove the air from the mercury as much as possible by most carefully boiling it. Figure 135 shows Beckmann's latest model for boiling and freezing point determinations. He further discusses the use of these thermometers as follows: The mercury may be transferred from the main container to the reservoir by heating in the vapor of the solvent, in an oil bath, or even with a little care, over a free flame. In order to break the mercury which has entered the upper part of the reservoir away from the capillary, the middle of the thermometer is grasped in the right hand with the reservoir upward, and the right hand struck against the other hand. Although the mercury adhering to the capillary is rather insensitive to shocks applied to the thermometer when perpendicular, nevertheless it is easy to detach mercury by tapping. If the capillary thread is not at the desired place on the scale when heated to the boiling point of the solvent, mercury is again jerked off, or added to the capillary by bringing a droplet of mercury of suitable size to the capillary by tapping, and then causing this to unite with that of the capillary by warming the bulb. Finally, it is customary to take up any droplets of mercury which have spurted on the walls of the reservoir into the main supply at its bottom.

In addition to heating, mercury can also be transferred to the reservoir by inverting the thermometer and lightly tapping its metal cap downward until the mercury in the bulb is detached from the glass wall at one place, and has been driven so far into the capillary, that of its own accord it will flow farther downward in it. If the thermometer is kept in this position, the reservoir will finally become completely filled. If the thermometer is then inverted with care, so that the mercury does not separate from the capillary, the mercury will again run out of the reservoir. Consequently, if mercury is to be removed from the reservoir, it is only necessary to invert and allow the mercury to flow from the bulb and to unite it with the part which has been thrown into the capillary, and then place the thermometer in the normal position. It is apparent from this how thermometers presumably rendered useless by shipment may be put in order. During transportation the reservoir may be completely filled by inversion and jarring, and subsequent shocks may break the capillary thread at the reservoir, and the mercury then flows back. Attempts have been made to unite the mercury by warming the bulb or the reservoir, but this usually damages the thermometer. This union is easily accomplished by inverting the thermometer and allowing the mercury to flow off.

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[11] Beckmann, E., *Z. ph. Ch.*, **15**, 672 (1894).

Beckmann also calls attention to the disturbances which may attend working below room temperatures. If, while its upper part contains mercury, the reservoir is heated more strongly on one side, by standing in the sun, for instance, the colder side gradually becomes covered with a deposit of mercury. Such distillation of the metal, of course, must change the setting of the thermometer.

There are many defects in the Beckmann method. Often it is not easy to attain the proper setting. These disadvantages are overcome by Kühn[12] by means of the design shown in the sketches in figure 136. Excess mercury is transferred into the two reserve arms without any tapping, by simply slanting the thermometer, and the flow of the mercury is favored by the lengthened capillary *a* (see the enlargement in fig. 136). The return is accomplished by the reverse motion, and by warming the lower mercury bulb until the mercury thread unites at the capillary opening *a*. The rough setting is made by means of the auxiliary scale, and the fine setting by counting the mercury drops falling from the opening, *a*, whose size in degrees, *c*, is etched on the scale of each thermometer. The mercury drops may be made to fall sooner, at will, by a slight shock, and settings within a few hundredths of a degree are easily made. Mercury drops of equal size may be made to fall by fastening the thermometer in a holder, and slowly warming the mercury bulb. The exit tip, *a*, is

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[12] Kühn, A., *Ch. Zt.*, **36**, 843 (1912); see also *Ch. Zt.*, **26**, 337 (1902).

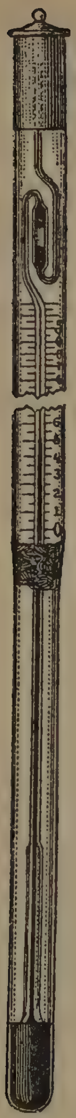

FIG. 135. THERMOMETER FOR MOLECULAR WEIGHT DETERMINATIONS (BECKMANN)

Actual size of scale 25 to 30 cm. long

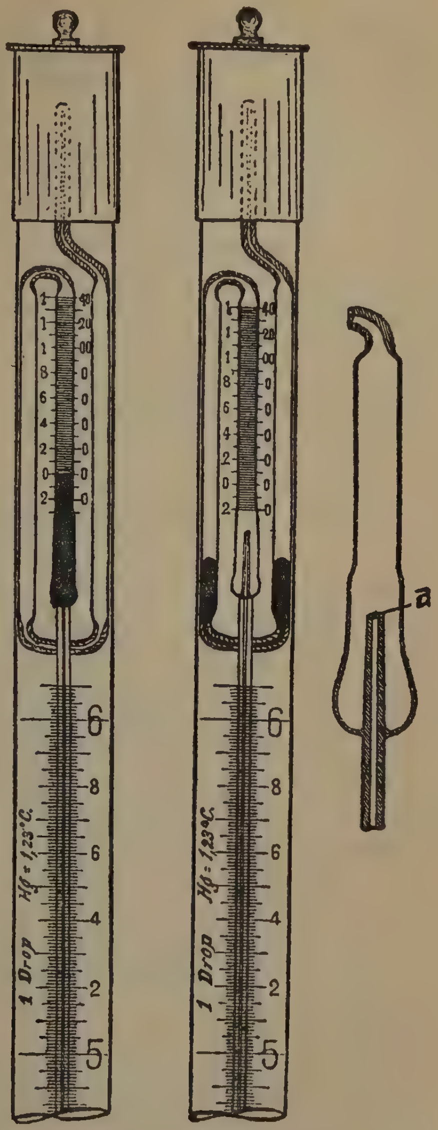

FIG. 136. BECKMANN THERMOMETER WITH KÜHN'S PRECISION SETTING (WITHOUT TAPPING)

constructed for about 1°C., as a rule, but it may be arranged for fractions of a degree. If the reservoirs have become filled during transportation, they empty automatically when the thermometer is set upright. The syphoning back of very small quantities of mercury can be dispensed with, because of the certain and exact settings made possible by the dropping device.

It may also be stated that, according to Aufhäuser,[13] the vertical position is particularly favorable for the fine thermometers, and consequently, it is best to store them in this position. This may be done by sticking their lower ends into a cork floating on water in a glass cylinder of sufficient height. The thermometers are safely held by a second cork at the top.

The views of Landsberger on thermometers are given under the discussion of his method involving the elevation of the boiling point.

DETERMINATION OF MOLECULAR WEIGHTS BY DEPRESSION OF THE FREEZING POINT

According to Beckmann

The apparatus, devised for this purpose by Beckmann,[14] has the following form (fig. 137). The vessel which contains the liquid to be tested, consists of a large thick walled test tube having a side arm through which the substance may be added. A determination is started by taring the test tube containing several sharp edged fragments of platinum. The test tube which up to the side arm, holds about 25 cc., is then charged with about 15 grams of solvent, the upper part dried with filter paper, and then weighed exactly to the nearest centigram. After the stirrer of thick platinum wire has been put in, the thermometer is fastened in place by means of a cork. A wider cylinder *B* which serves as an air jacket, is fastened around the test tube with a cork and immersed in a battery jar filled with the cooling liquid.

It is better to keep the temperature in the battery jar about 2 to 5° below the freezing point of the liquid to be tested. When working with glacial acetic acid, if the temperature is too high, it may be lowered by adding pieces of ice and agitating with an external stirrer. If benzene, melting at about 5.5° is being used, the battery jar is almost filled with pieces of ice which are then covered with water. With enough ice, there need be no worry as to the external temperature, unless the freezing point of the solution to be tested, falls below 2°. If stronger cooling is necessary, which of course, is the case when water is used, sufficient sodium chloride to produce the desired temperature is stirred into the mixture of ice and water in the outer vessel. It is not necessary that the freezing vessel be visible at all times. After some experience, there is no need of observing the outer temperature by a thermometer. This may be judged by the rate at which the temperature in the inner vessel falls.

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[13] Aufhäuser, D., *Z. f. chem. Apparatkunde*, **1**, 226 (1905).

[14] Beckmann, E., *Z. ph. Ch.*, **2**, 639 (1888).

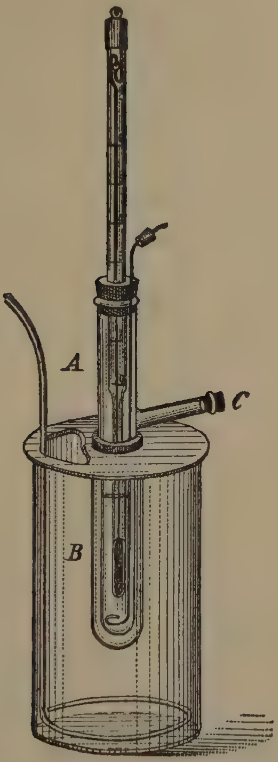

Fig. 137. Apparatus for Determining the Lowering of Freezing Point

After the liquid has been cooled below its freezing point, pains should be taken to insure the beginning of crystallization. With constant stirring, the mercury of the thermometer rapidly rises, and its highest position indicates the freezing point. At first, it was customary to start crystallization by adding some frozen solvent, but it is obvious that this involves considerable difficulty. It is very inconvenient to add a small particle of solid benzene or water at a given time to the freezing vessel even at ordinary room temperature, and in midsummer, glacial acetic acid offers the same difficulty. Larger particles increase the quantity of solvent to an extent which is difficult to control, and consequently, attempts were made to avoid the introduction of any crystals. Later, particles of platinum were placed in the test tube which was also provided with a vertically acting stirrer, to overcome supercooling of the solvent as much as possible. When using benzene, this was very successful, and the mercury falls only a few hundredths of a degree below the freezing point, which is rapidly established, following a slight separation of very small crystals. Under the same conditions, glacial acetic acid may be supercooled somewhat more, *i.e.*, up to 0.5°, and water as much as 1°. In the last two cases, the greater quantity of ice separating is of no import when determining the freezing point of the pure solvent.

After the freezing point of the solvent has been determined in this way, and its constancy tested by repetition, and after the ice has melted, the material to be investigated is added through the side arm. Any particles adhering to the walls are washed down by tipping the test tube. After the sample has dissolved, the freezing point is determined twice. The depression is obtained by simple substraction. A further quantity of the substance may be added and the determination continued for higher concentrations.

When investigating solutions the necessity always arises, with increasing concentration, of avoiding as much as possible, excessive supercooling, *i.e.*, of limiting the quantity of solvent freezing out. Since the solvent alone separates, its removal results in the remaining solution being more concentrated, and this will always have a lower melting point. In this procedure possible errors become greater if, and this is particularly true when glacial acetic acid or water are used, the separation of crystals is retarded by the solute to a considerable extent, and this under certain circumstances, may amount to many degrees. But even in these cases, a high degree of accuracy may be reached without adding ice. After the separation of ice has been accomplished by cooling without an air jacket, but with vigorous stirring, the tube is allowed to stand quietly until a thin layer of the solvent freezes to the bottom of the test tube. The finely divided ice floating in the liquid disappears completely because it melts much more readily than the thin crust of ice. Further heating is interrupted by replacing the test tube in the air jacket and cooling liquid, and when the thermometer begins to fall, the determination is carried out as before. After a little practice, it is easy to proceed so that enough finely divided ice separates with a supercooling of 0.1° or a smaller fraction of a degree, to cause the thermometer to rise again. Gross errors in these determinations may not be avoided by relying entirely on the movement of the mercury thread. The observation should not be regarded as certain, until the separation of finely divided ice is actually seen.

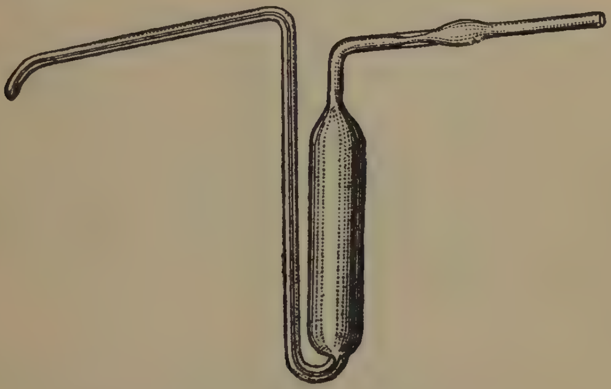

FIG. 138. FILLING PIPETTE (BECKMANN)

Liquids are added by means of Beckmann's apparatus shown in figure 138. It is filled by dipping the capillary, which is fused to the bottom of the cylindrical chamber, into the liquid; connecting the upper bent tube with a calcium chloride tube as a guard against moisture, and then applying suction. The material is discharged by blowing into the apparatus while the capillary is pushed into the side arm. The mouth of the capillary is bent downward and ground off at an angle, so that drops will not hang on it. Very volatile liquids may be kept from vaporizing if a very narrow capillary is used, and if the upper tube is drawn out, at one point, to a capillary as shown in the figure.

The determination itself

The molecular weight is determined as follows: The thermometer is set for the solvent in question, say benzene, *i.e.*, care is taken that when the thermometer is in freezing benzene, the mercury thread is about 0.5° from the upper end of the scale. About 15 grams of benzene is then put into the test tube and the battery jar is rather well filled with ice and water. The cooling is quite uniform because of the layer of air surrounding the test tube, if the benzene is agitated by the stirrer from time to time. Finally the temperature sinks below the freezing point of the benzene and it begins to solidify, if it is now stirred vigorously, and at the same time the temperature rises somewhat. The highest temperature, which is the freezing point of benzene, is read with the aid of a magnifying glass. The test tube is now removed from the cooling bath, and in the case of benzene, the heat of the hand is sufficient to melt the ice. The freezing point is determined again, and then a third time. The difference between these readings should not be more than 0.005°.

The determination of the depression of the freezing point is carried out in stages by adding the material to be investigated, little by little to the solvent, and determining the freezing point after each addition.

The molecular weight may be calculated from the equation: $M = c \cdot \frac{p}{t}$, in which M = the molecular weight sought; c = the constant of the solvent used; p = the per cent of solute in the solvent; t = the depression of the freezing point expressed in degrees C.

The constants of the commonly used solvents are:

Formic acid	27.7
Benzene	50.0
Diphenylamine	88.0
Glacial acetic acid	39.0
Naphthalene	69.0
Naphthylamine	78.0
Palmitic acid	44.0
Phenol	72.0
Water	18.5

The choice of solvent should be such that it has no chemical action on the material whose molecular weight is to be determined. Benzene, glacial acetic acid and phenol usually suffice for most laboratory experiments. It may be said with regard to phenol that somewhat different figures are obtained with coal tar phenol than with the synthetic product, probably because the constant of even the purest carbolic acid does not agree with that of synthetic phenol.

When using phenol (freezing point 40 to 42°), particularly recommended by Eykman,[15] the cooling vessel filled with water at 35 to 37°, is put on an asbestos plate, and the temperature is kept about 3 to 6° below the freezing point by means of a small flame. The phenol in the test tube is melted over a free flame and is then brought to the solidification point by immersing it directly in the cooling water, while stirring it constantly. Excessive supercooling usually does not occur. After reading the approximate solidification temperature, the contents of the tube are stirred over a flame until all but a very small portion of the crystals have melted and the cooling is allowed to proceed in the air jacket. Care must be taken that the crystal particles still present are not all melted, or resolidification without inoculation with phenol crystals, will probably not occur. The phenol must be stirred occasionally while cooling, and the stirring temporarily increased somewhat as soon as the temperature has fallen to the vicinity of the freezing point. While slow stirring is continued, the mercury quickly rises to a maximum, the freezing point, and stays there for some time.

TABLE 8

Quantities of materials and accuracy of Beckmann's investigations

PER CENT CONTENT OF SOLUTION	FREEZING POINT DEPRESSION	CALCULATED MOLECULAR WEIGHT	PER CENT CONTENT OF SOLUTION	FREEZING POINT DEPRESSION	CALCULATED MOLECULAR WEIGHT
Acetone $(CH_3)_2CO = 58$			Benzaldehyde $C_6H_5CHO = 106$		
0.473	0.405	57.2	0.511	0.245	102
1.458	1.220	58.6	2.093	1.000	103
4.592	3.615	62.2	6.879	3.130	108
7.162	5.365	65.4	12.180	5.245	114
Acetophenone $C_6H_5COCH_3 = 120$			Benzophenone oxime $(C_6H_5)_2C = NOH = 197$		
0.948	0.405	115	0.237	0.055	211
4.001	1.650	119	0.525	0.115	224
8.085	3.235	123	0.782	0.160	239
14.170	5.425	128	1.563	0.295	260

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[15] Eykman, J. F., *Z. ph. Ch.*, **2**, 964 (1888).

The quantities in which the material being investigated, were added in about 4 portions, as well as the accuracy attained, may be seen from the figures given by Beckmann[16] in table 8. Benzene was the solvent.

Introduction of the sample

Liquids may easily be introduced into the apparatus by means of the pipette discussed above. The number of drops allowed to run in is an indication of the weight (see page 1). Solid materials are best formed into rods by means of a small press, and pieces of these may be weighed and dropped into the apparatus. Gernhardt constructed the hand pastil press shown in figures 139, 140, 141, which Beckmann[17] has found satisfactory for all laboratory needs. The materials should be compressed no more than necessary, so that the rate of solution is lowered as little as possible. For sensitive materials, Beckmann had the metal parts of the presses replaced, according to need by porcelain or glass or else by ivory or ebonite.

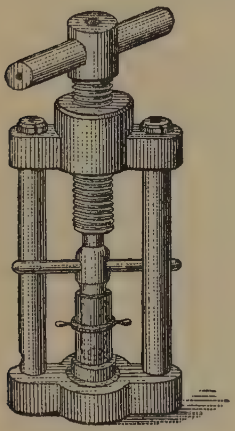

FIG. 139. TABLET PRESS

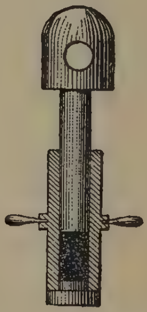

FIG. 140. PRESSING THE SUBSTANCE

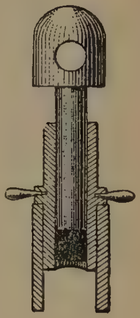

FIG. 141. EJECTING THE TABLET

It is obvious that it is most important that complete solution take place, and it is permissible to apply heat for this purpose, since even if any small quantity of mercury enters the reservoir it will not be detached from the thread, as stated in the discussion of thermometers.

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[16] Beckmann, E., *Z. ph. Ch.*, **2**, 717 (1888).
[17] Beckmann, E., *Z. ph. Ch.*, **15**, 671 (1894).

If materials may be melted without decomposition, they may be made into rods by the procedure given under the determination of vapor density by displacement of air.

If it seems necessary to introduce the material as a powder, this is best done after enclosing it in platinum gauze. A small capsule is made of close-meshed platinum gauze, weighed and the substance introduced with the aid of a small tube widened above to form a funnel. It is pushed through the funnel by a wire. The top of the gauze is folded together and the capsule reweighed. In case of necessity, the powdered material may be introduced directly into the freezing point apparatus from a weighing tube of sufficient length which is emptied by turning and tapping. Or the rear end of the weighing tube may be closed with a glass rod which can be pushed forward. Any material adhering to the tubulure may then be removed by rinsing it with the solvent.

Concluding remarks

This method almost always gives satisfactory results, which deviate by about 5 per cent from the anticipated molecular weight. If, as sometimes happens, the values found are only about half as great as those expected, the determination should be repeated with a different solvent. Even though there is no question as to chemical action of the material upon the solvent, cases do occur in which the figures obtained do not agree with the molecular weight of the material.

The apparatus described above suffices for practically all cases because it permits rapid working and consequently, no appreciable error is introduced because of the hygroscopicity of the solvent used. The freezing point of liquids is often found to be too low when exposed to ordinary air, because small quantities of water are absorbed from it by the solvent. The first apparatus described suffices for materials which dissolve rapidly and produce depressions of 0.2° or more, and this can usually be arranged for. If a material dissolves very slowly, perhaps in fifteen to thirty minutes, and to such a slight extent that the depression is less than one-tenth or two-tenths of a degree, it is absolutely necessary to exclude atmospheric moisture.

Beckmann[18] has devised apparatus in which the entrance of moist air is hindered by a counter current of dry air (fig. 142). The centigrade thermometer *D* and the vertical part of the drying tube *F* are fastened by means of a soft rubber stopper into the widened upper end of the freezing tube *A*. The stirrer *E* passes through this part

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[18] Beckmann, *Z. ph. Ch.*, **7**, 324 (1891).

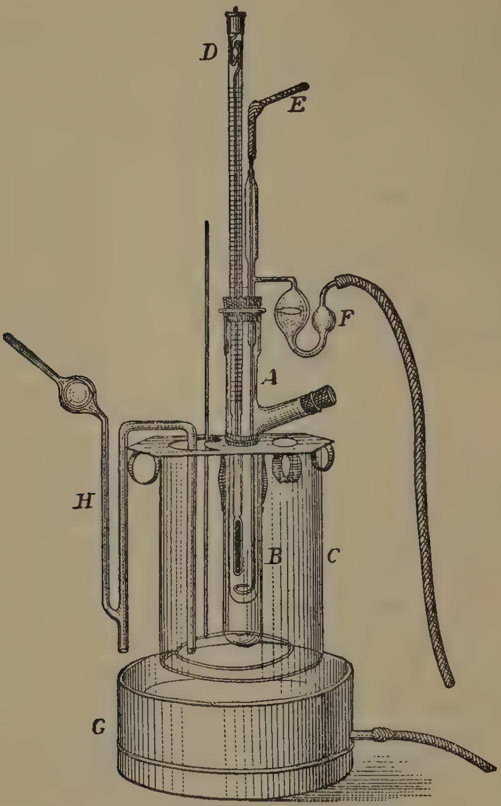

Fig. 142. Apparatus with Arrangement for Exclusion of Atmospheric Moisture (Beckmann)

of the drying tube, fitting it rather well, though it may be moved up and down without much friction. It consists of a thick platinum wire, or for economy's sake, of a glass rod to whose lower end a stout platinum wire ring is fastened with sealing glass. As a handle, a piece of rubber tubing such as would be easily obtained by removing both ends from a piece like that used in the well known Friedländer models for showing the direction of the valences of the carbon atom,[19] is slipped over the upper end. The apparatus may be closed during a long interruption of the experiment, by simply slipping the rubber tube over the upper end of the tube *F*.

The solvent may be weighed or pipetted into the freezing tube either before or after connecting the devices named. In the latter case, it is added through the side tube, which is closed with either cork, rubber or glass, depending upon the solvent. In case the stirrer does not move freely and does not run parallel to the thermometer, the vertical tube of *F* is brought into the correct position by inserting a piece of cork or by drawing it toward the thermometer by a cord or a rubber band.

Enough concentrated sulfuric acid[20] is put into the bulb tube to fill the connections between the bulbs, and a current of dry air is drawn through just too fast to count the single bubbles, all the while the determination is being carried out according to the directions given above. The spurting of sulfuric acid from the larger bulb is made impossible by a protective glass baffle plate which is sealed in it. The widened part of the upper vertical portion of *F* is designed to hold a small reserve of dry air for the better protection of the freezing tube. The current of air may be produced by Beutell's bellows as modified by Bömer,[21] but any water blowing drum may be used. The air leaving the bellows passes first through two ordinary drying towers filled with pumice and sulfuric acid, and then enters the bulb tube through a long rubber tube which permits the freezing tube to be freely moved. The sulfuric acid in *F* retains the small quantities of water which have entered the rubber tube by diffusion or other means.

The earlier apparatus has undergone the following additional modifications for reasons of convenience. These are shown in figure 142. The metal cover of the battery jar has four weak clamps riveted to it, to hold down the air jacket *B* after removing the freezing vessel, and four metal rings which make it easier to take it off and replace it. This makes it very convenient to take the main portions of the apparatus out of the cooling liquid and to place them on any tripod or ring stand. Ice and water may be easily added through the larger opening in the side of the cover, and the smaller side opening serves especially for introducing a thermometer or the inoculating pencil mentioned below. The central opening through which the air jacket passes has its edges rounded to prevent breaking the glass edge; a rubber ring protects the air jacket in the same way. A syphon *H* is intended to run off the cooling liquid, and the base *G* catches any overflow. When using low temperatures, it is well to surround the battery jar *C* with a poor conductor of heat, such as felt.

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[19] Meyer, Victor, *Ber.*, **23**, 572 (1890).

[20] This is best removed from the supply bottle with a pipette, since the acid on the neck of the bottle often contains considerable water. Before each new series of experiments the bulb tube should be rinsed with water and alcohol, ether, air drawn through it and then charged with fresh acid.

[21] Bömer, M., *Z. f. angew. Chem.*, **2**, 390 (1889). A syphon action of the wide exit tube may be easily avoided by having an opening on a side tube at the highest point.

The efficiency of this arrangement is easily tested by repeatedly determining the freezing point of glacial acetic acid during a period of fifteen to thirty minutes or more. It should be constant within the small variations inherent in all temperature determinations made with a mercury thermometer, when only the mercury reservoir is immersed.

The use of glacial acetic acid as solvent was particularly recommended and deservedly so, by Victor Meyer and K. Auwers,[22] and its hygroscopic properties are no longer a detriment for even very accurate determinations (see the method of Meyer and Jaeger below). The results are not markedly affected by the small quantities of moisture entering the apparatus while introducing the material through the side tube.

The dry air passed through can, of course, be freed of carbon dioxide, or it may be replaced by any other desired gas, such as nitrogen, hydrogen, carbon dioxide, if the nature of the solution makes this desirable.

Any error arising from evaporation of the solvent (benzene, water, glacial acetic acid, for instance) usually need not be considered. The losses are very slight at the freezing temperature, and should 0.1 gram of the solvent evaporate, the error introduced when 10 grams of the solvent are used, would be negligible in comparison with the allowed error of more than 5 per cent in molecular weight determinations.

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[22] Auwers, K., *Ber.*, **21**, 707 (1888).

An ordinary thick walled test tube without a side arm often suffices as a freezing vessel for aqueous liquids. The increase of liquid from condensation of atmospheric moisture appears to be just as inconsiderable as the evaporation.

Before introducing the substance into the freezing tube, through the side arm, the stirrer is turned to one side by moving the upper stopper so that there is free access to the tube. Any of the sample in the side arm may be brought into solution by filling it with solvent by tipping the freezing tube. Particles of the material which may have adhered to the stirrer and thermometer are washed down by the liquid flowing out of the side arm when the tube is again turned upright. Powders which are difficult to introduce should be pressed into pastils.

DETERMINATION OF MOLECULAR WEIGHT BY BOILING POINT ELEVATION

(*a*) *Landsberger's Method*

Beckmann was likewise the first to make practicable molecular weight determinations by elevation of the boiling point. Throughout many years of activity he constantly improved his apparatus.[23] However, Landsberger's exceedingly simple apparatus for solvents which do not boil too high, suffices for the molecular weight determinations required by organic laboratories. Therefore, a detailed description of it is given here. To this will be added a discussion of a modification of the apparatus, designed for glacial acetic acid which dissolves so many substances.

Landsberger[24] heats the solvent used in the determination of the molecular weight, to its boiling point, solely by a current of its own vapor. If the vapor comes in contact with the cold liquid, most of it condenses, and the latent heat set free raises the temperature of the liquid. This condensation continues to a considerable extent until the liquid has been heated to its boiling point. After this has been reached, only enough vapor will condense as is necessary to compensate for the heat lost by radiation and conduction. The temperature then will not fall below the boiling point, provided that a comparatively uniform introduction of vapor is continued. On the other hand, the solvent cannot be superheated, since a pure liquid

[23] Beckmann, E., *Z. ph. Ch.*, **53**, 137 (1905).

[24] Landsberger, W., *Ber.*, **31**, 459 (1898).

can be heated only to its boiling point by its vapor. The quantity of vapor condensing, and the time elapsing until the liquid reaches the boiling point differs, under the same conditions, for different liquids, and is of course, dependent on the latent heat of vaporization, the specific heat of the liquid, and the difference between the boiling point and room temperature. However, if the quantity of liquid to be heated is small, the amount of liquid condensed, as well as the time necessary, will also not be great, since the latent heat of condensation of all liquids is considerably greater than the specific heat.

Landsberger has arranged his apparatus as follows: The real boiling vessel *a* (fig. 143), is an ordinary test tube 3 cm. internal diameter and 16 cm. high. It has an opening *b*, 2 cm. from the top. It is closed by a two-hole cork *c*, one of whose openings is intended for the thermometer, while a glass tube *e*, bent twice at right angles passes through the other. The longer arm of the tube *e* is cut off at an angle on the side toward the observer and also on the opposite side, as shown in figure 143, *e*, so that the vapor may pass out of it uniformly in all directions with as little resistance as possible. The vapor, which is generated in a round bottom flask *f* having a capacity of 250 to 500 cc., is led in through this tube. The flask is closed with a two-hole cork *g;* a safety tube passes through one opening, and the shorter arm of *e*, which is also cut off at an angle, goes through the other. The boiling vessel *a* is connected by means of a cork *h* with the second test tube *i*, 19 cm. high and 4.5 cm. internal diameter, and this has a slanting glass tube *k* sealed on, about 2 cm. from the top. This is connected with the condenser *l*, by means of a cork or a small piece of rubber tubing. By this arrangement, the vapor which has passed through the liquid issues from the boiling vessel into the outer test tube where a part condenses, while most of it is liquefied in the condenser and collected in the receiver *m*. The condensation of the vapor in the inner tube is diminished by surrounding the boiling vessel with a vapor jacket. (When working with water, the condenser may be omitted, and the steam allowed to escape directly into the atmosphere.)

Although the Beckmann thermometer is very good for these determinations, nevertheless Landsberger prefers a thermometer 22 cm. long divided in 0.5°, having a range of about 10°. The capillary of this thermometer also is widened at the upper end so that a small quantity of mercury may be detached if necessary. These thermometers may easily be read with a magnifying glass to within several thousandths of a degree, which is sufficient. Furthermore, these small thermometers may be set more rapidly than the large ones of the Beckmann type. Finally, the loss is less if one of them is broken.

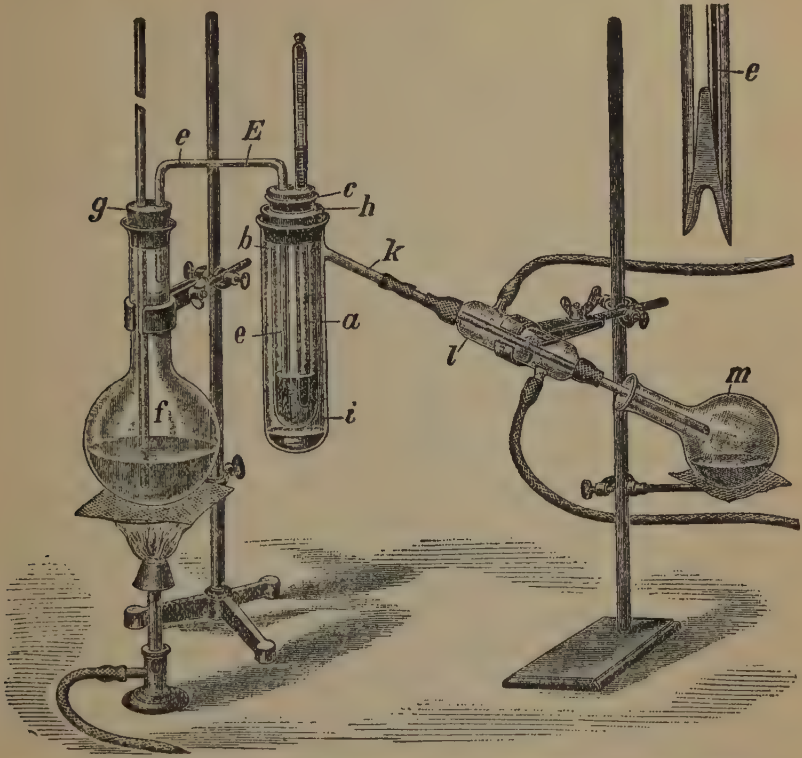

FIG. 143. LANDSBERGER'S APPARATUS FOR THE DETERMINATION OF MOLECULAR WEIGHTS, WITH EXPERIMENTAL ARRANGEMENT FOR THE USE OF ALCOHOL, BENZENE (WATER) AS SOLVENTS

One-sixth actual size (the condenser has been reduced in drawing)

A molecular weight determination is started by placing in the boiling vessel, *a*, only enough solvent so that the bulb of the thermometer will just be covered by the liquid toward the close of the experiment. This requires:

	cc.
Ethyl ether	about 7
Carbon bisulfide	about 7
Acetone	about 4
Chloroform	about 4
Ethyl alcohol	about 5
Benzene	about 6
Water	about 7

The cork *c* is then inserted so that the tube *e* touches the bottom of of the vessel, the thermometer *d* is put in place and the jacket *i* is put around the test tube. The flask *f* is charged with about 250 cc. of solvent and 2 pieces of porous plate are added to make the boiling uniform. (If only a small quantity of liquid is available 100 to 125 cc. will suffice.) The writer found it advantageous to cut the tube *e* at *E*, and to reconnect it by a rubber tube. If the solvent is not very valuable, it is well to make this connection after the boiling has begun and when most of the air has been expelled from the boiling flask. If this is done, this air does not enter *a*, where at first it would hinder the attainment of a constant boiling point.

The liquid is boiled either by direct heating with a flame (alcohol, water and benzene as solvents) or by placing the flask in a heated water bath from which the burner has been removed. If the flask is placed in the bath to that the level within and without is about the same, the initial temperature of the bath should be approximately 70° when ether is the solvent, about 80° for carbon bisulfide and 100° for acetone and chloroform. There is practically no danger from the breaking of a round botton flask, if the flame is not allowed to touch it, but is kept away from it by the interposition of two narrow wire gauzes on a ring about 2 cm. below the flask. Landsberger completed a large number of experiments using alcohol and benzene as solvents, without damage to the flask.

After the condenser water has been turned on, and the small Bunsen burner, fitted with a chimney, has been lighted, or the generating flask has been placed in a water bath heated to the proper temperature, the tube *e*, of the boiling apparatus is pushed through the free opening of the cork *g* carrying the safety tube, and the side tube *k* is connected with the condenser *l* by a cork or a short rubber tube.

As soon as the solvent in the generator boils and most of the air has been expelled, the vapor passing through the tube *e* will condense, and the temperature of the liquid in *a* will rise rapidly until it finally attains a constant value. It is advisable to read and record the temperature every fifteen seconds so that the course of the temperature may be followed from the figures, and thus there will be no doubt as to the constancy of the boiling point. This, as a rule, is attained in from two to six minutes from the beginning of the condensation and the experiment is interrupted when there has been no change in temperature for one and one-half minutes. Because of the brevity of this experiment, it is best to check it by repetition, particularly if the operator has had little experience with this method or is using a new solvent. The liquids in all of the vessels are then added to the solvent which has not been used. They are shaken together and the apparatus is filled and started as before. The used pieces of clay plate should be replaced by new ones. If the technique has been correct and if the barometer reading has not changed in the meantime, the same boiling point will be found.

After the boiling point of the pure solvent has been determined with certainty, all of the solvent is again poured together and the apparatus is filled and started exactly as described above, with the exception that a sample of the substance, which has previously been weighed to within 1 mgm. in a small glass tube, has been added to the boiling vessel *a* and any particles of the substance adhering to the weighing tube washed into the boiling flask *a*, with the proper quantity of solvent. The temperatures are observed if possible every eighth of a minute, and the experiment is interrupted as soon as three consecutive readings are the same. This is done by breaking the connection with the condenser, withdrawing the glass tube *e* from the cork *g*, and removing the outer vessel *i* together with the stopper *h*. The opening *b* and the open end of the tube *e*, are closed with two small rubber stoppers held in readiness, the outside of the apparatus cleaned, and the apparatus hung in a wire sling and then weighed to centigrams, together with the glass tube and thermometer.

The apparatus is then cleaned, usually by rinsing with alcohol and ether, dried, and weighed together with the rubber stoppers in the same sling.

If the weight of the material is substracted from that of the solution, *i.e.*, the difference between the two weighings taken, the weight of the solvent is obtained, and it is easy to calculate the quantity of material dissolved in 100 grams of the solvent (per cent content). This per cent content is multiplied by the constant which has been ascertained for every common solvent, and then divided by the elevation of the boiling point, and the result is the molecular weight of the material being investigated.

According to Landsberger, 1 gram molecule in 100 grams of solvent raises the boiling point of:

Acetone	16.7°
Ethyl alcohol	11.5°
Ethyl ether	21.1°
Benzene	26.7°
Chloroform	36.6°
Carbon bisulfide	23.7°
Water	5.2°

Thus he found that 0.5469 gram naphthalene dissolved in 7.15 grams ethyl ether raised the boiling point 1.24°. The concentration of the solution is calculated to be 7.65 per cent and $\frac{7.65 \times 21.1}{1.24} =$ 130. This figure is the observed molecular weight, while 128 is the theoretical figure calculated from the formula $C_{10}H_8$

(b) *Modification of Landsberger's Method by Meyer and Jaeger*

The Landsberger method in the form given above is only suited to low boiling solvents. Meyer and Jaeger[25] have modified it so that it may be applied to higher boiling liquids, especially to glacial acetic acid. This solvent offers particular advantages, first, because it dissolves many materials which do not dissolve at all or not enough in other liquids, and, secondly, because it is one of those solvents in which the boiling point methods[26] do not yield abnormal molecular weights because of association.

The difficulties of using glacial acetic acid in the Landsberger procedure are due, in part, to the considerable difference between the boiling point of the acid and the temperature of the air, and in part to its extreme hygroscopic properties which seem to be even greater than those of anhydrous alcohol. The consequence is that if the determination is carried out in the ordinary way, too much acetic acid condenses in the boiling vessel so that the experiment can never be carried to a finish; and, further, a constant temperature when

[25] Meyer, Richard, and Jaeger, Paul, *Ber.*, **36**, 1555 (1903).

[26] Beckmann, E., *Z. ph. Ch.*, **6**, 449 (1890).

determining the boiling point of the pure solvent can be attained only with difficulty, if at all. After overcoming numerous difficulties, they evolved an apparatus differing from Landsberger's in the following particulars:

(1) The jacket surrounding the boiling vessel is charged at the start, with a larger volume of the solvent, and this is heated to boiling. Consequently, the liquid in the boiling vessel is heated almost to the boiling point even before the entrance of the heating vapor, and the loss of heat to the outside during the experiment is almost completely eliminated.

(2) The cold air in the vapor generator is expelled into the outer air by the vapors of the solvent before the start of the real experiment, so that it does not enter the boiling flask at all, and consequently, cannot cool it.

(3) Instead of determining the boiling point of the pure solvent, they observed that of a solution containing a known quantity of the material under investigation, *i.e.*, the boiling points of two solutions of different concentrations are determined. This procedure proved very advantageous, since in both cases, the thermometer sinks again after reaching the maximum temperature. The reason is that the original solution is diluted because of the condensation of the acetic acid vapors. In the first stage of the experiment the heating effect of the entering vapors predominates; but when this has reached its maximum, the introduction of more vapors must cause the temperature to fall because of the progressive dilution. The point at which this occurs is easily and definitely ascertained.

(4) Precautions are taken to hinder the absorption of moisture or else to render its effects harmless.

The apparatus (fig. 144) is arranges as follows: A well ground glass cock *e* is inserted in the tube *d*, which is bent twice at right angles; the cork of the vapor generator *a*, instead of a safety tube, carries an air condenser *b* whose top is widened and which communicates with the outer air through a glass cock *c*, and the calcium chloride tube *m*. The receiver is an ordinary suction flask *k*, connected air tight with the condenser, and its side arm has a calcium chloride tube *l*. The condensation in the distilling tube *d* is prevented as much as possible by wrapping it with a woolen band. They used a thermometer having the interval from 111 to 122° divided into twentieths of a degree, and read it with a magnifying glass.

Bunsen burners fitted with a chimney, gas and air regulators, are used for heating. Finally, they found it well to protect the apparatus from the currents of heat and drafts of air emanating from the observer, by a heavy pane of plate glass placed before it, and to set up the whole apparatus in a very quiet place.

The molecular weight is determined as follows: The empty apparatus, comprising the boiling vessel *f*, the thermometer *h*, and the tubes *d*, and their corks, is weighed first. All of the corks are boiled out in glacial acetic acid before being used. The open end of *d*, as well as the opening *g* is closed by small corks during this, and the following weighings. The weighed sample I and 3 to 4 cc. glacial acetic acid are then placed in the vessel *f*. The glacial acetic acid should be 99 to 100 per cent. The vessel *f* is then placed in the boiling jacket *i* which contains about 75 cc. glacial acetic acid and

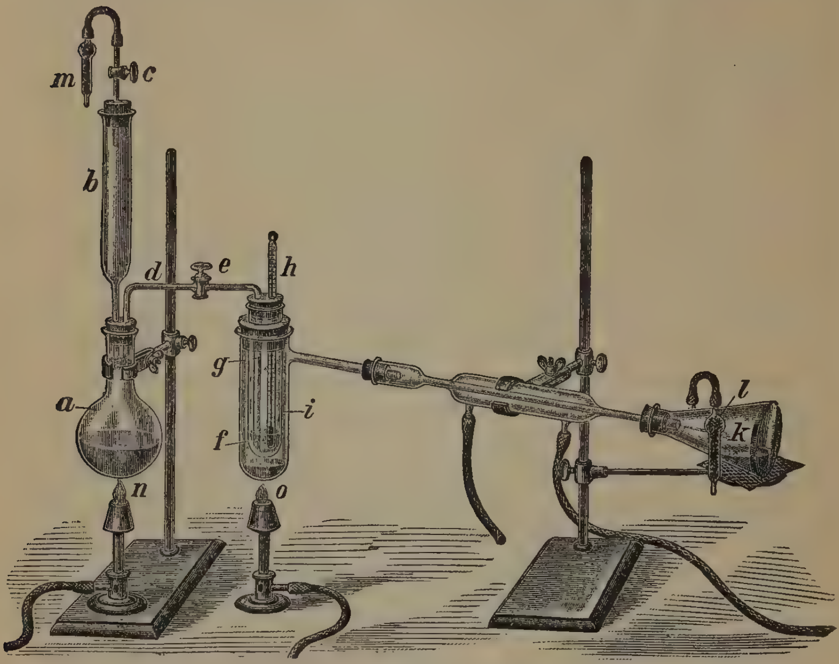

FIG. 144. DETERMINATION OF MOLECULAR WEIGHTS (MEYER AND JÄGER). EXPERIMENTAL ARRANGMENT FOR USE OF GLACIAL-ACETIC ACID (ANILINE) AS SOLVENT

a few fragments of pumice. The flask *a* is charged with 200 to 250 cc. glacial acetic acid and about 10 grams of copper sulfate, dehydrated at about 300°, together with some pumice particles. About 10 grams anhydrous copper sulfate is placed in the receiver *k*. The two slightly lubricated cocks *c* and *e* are closed at first. While the glacial acetic acid in the boiling jacket *i* is being heated to boiling, sample II is weighed out. As soon as the temperature in *f* has almost reached 118°, the boiling point of acetic acid, the heating of the flash *a* is begun, the calcium chloride tube *m* being removed and the cock *c* opened. The contents of *a* must finally boil vigorously so that the vapors condense in the upper part of *b*. The two cocks are then turned, *i.e.*, *e* is opened, *c* is closed. At first, the temperature in *f* falls several degrees—undoubtedly because of the entrance of the air still remaining in the tube *d*—but it immediately rises again and rapidly reaches a maximum, and then falls again immediately. At this instant, the cock *e* is closed quickly, *c* is opened, the flames removed, the calcium chloride tube *m* reconnected to *c*, and the maximum temperature recorded. The apparatus is allowed to cool with the cock *e* closed, and is then weighed. The sample II is then added to solution I in the apparatus, and the procedure repeated. After the maximum has been recorded, the apparatus is weighed again.

The calculation of the molecular weight of acetanilide in glacial acetic acid may be cited as an example to show how the results of the experiment may be used. The two samples are indicated as s_1 and s_2; the quantities of solvent as l_1 and l_2; the temperature maxima as t_1 and t_2. The molecular boiling point elevation, K, of acetic acid is 25.3.

$s_1 = 0.5176$ gram. Apparatus $+ s_1 + l_1 = 135.88$
Apparatus empty $= 124.12$
$s_1 + l_1 = 11.76$
$- s_1 = 0.52$
$l_1 = 11.24$
$s_2 = 1.0844$ gram. Apparatus $+ s_1 + l_1 + s_2 + l_2 = 144.55$
Apparatus $+ s_1 + l_1 = 135.88$
$s_2 + l_2 = 8.67$
$- s_2 = 1.08$
$l_2 = 7.59$
$s_1 + s_2 = 1.6020$ gram. $l_1 + l_2 = 18.83$ grams
$t_2 = 119.245°$
$t_1 = 118.510$
$t_2 - t_1 = \Delta = 0.735$

The concentration of the solution in the first experiment is now recalculated to the total quantity of solvent present during the second experiment.

to $(l_1 + l_2)$ gram solvent there are at first:

$$\frac{(l_1 + l_2)s_1}{l_1} = \frac{18.83 \times 0.5176}{11.24} = 0.8671 \text{ gram substance.}$$

If this is substracted from the total quantity of substance used, the result is the quantity of substance which caused the elevation of the boiling point from the first to the second figure:

$$s_1 + s_2 - \frac{(l_1 + l_2)s_1}{l_1} = 1.6020 - 0.8671 \text{ gram} = 0.7349 \text{ gram}$$

This figure is used as s in the formula for calculating the molecular weight

$$m = \frac{100 \cdot s \cdot K \cdot}{l \cdot \Delta}$$

in which $l = l_1 + l_2$. Consequently:

$$m = \frac{100 \times 0.7349 \times 25.3}{18.83 \times 0.735} = 134.5. \quad \text{Calculated, } m = 135.$$

The determinations in acetic acid, published by them, almost without exception, show an agreement in the figures which can hardly be achieved by other methods of determining molecular weights.

It may be noted that they have also carried out molecular weight determinations in this apparatus, with aniline as solvent.

DETERMINATION OF MOLECULAR WEIGHT WITH THE AID OF THE MICROSCOPE

According to Barger

Barger's method of determining molecular weights which is based upon an entirely different principle will be included here.[27] It is founded on the comparison of the vapor pressures of two solutions.

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[27] Barger, G., *J. Chem. Soc.*, **85,** 286 (1904); see also Barger, G., *Ber.*, **37**, 1754 (1904).

The measurements are made on biconcave lens like drops in a capillary tube. A difference in the vapor pressures brings about a reciprocal change in the size of the drops, and this may be measured microscopically by means of an ocular micrometer. Only about 0.5 gram of material is required. The second solution, whose concentration must also be known, is made from a compound of known molecular weight (cane sugar, benzil, azobenzene). The solvent need not be pure; 90 per cent alcohol, petroleum ether (boiling point 50 to 60°) may be used. Of course, both solutions must be made from the same lot of the solvent. The quantity of material to be investigated, as well as of solvent, are almost a minimum, and with their aid, Barger found the molecular weight of glucose, which is 180, to lie between 179 and 192. He found 131 to 146 instead of 138 for the molecular weight of salicylic acid.

CHAPTER XV

COMMINUTING AND MIXING SUBSTANCES

PULVERIZING AND FINELY DIVIDING SUBSTANCES

Ordinarily, not enough attention is paid to the value of finely dividing materials which are to react with each other. In organic chemical laboratories, substances are usually pulverized in porcelain mortars, but these have the disadvantage of being of little use for hygroscopic, as well as poisonous, materials. When working with the former, it is impossible to prevent absorption of moisture from the air, and with the latter, the inhalation of dust is a matter of considerable concern, for instance, with potassium cyanide and many alkaloids.

When Scholl[1] found it necessary to grind aluminium chloride, while excluding the air, he avoided these difficulties very successfully by enclosing the mortar with an air tight rubber cap, which had a small circular opening in the middle through which the pestle could be inserted. In this way, the aluminium chloride, for example, whose unpleasant hygroscopic properties are known to everyone who has worked with it, could be ground as long as desired, with complete exclusion of air.

Rinck and Kossel[2] have described an apparatus for finely dividing animal materials. Only reference will be made here to this.

To bring about a thorough reaction of the halogens (and of other reagents) on solids, it is not only essential to finely pulverize the latter, but according to a private communication from E. Fischer, they must be passed through the finest of sieves, as is customary in preparing samples for mineral analysis.

The following observation of Fischer[3] is given to show the influence of the finely divided state of material, if the course of reaction is dependent on it. After the failure of many attempts to convert ordinary glycocoll, crystallized from water, into the hydrochloride of the chloride, $HCl \cdot NH_2 \cdot CH_2 \cdot COCl$, an accidental observation led to the correct method. It was only necessary to dissolve the glycocoll in a little warm water, and to precipitate it rapidly by a large excess of absolute alcohol. This product was carefully dried at 100°, pulverized and passed through a fine hair sieve. If 10 grams of the amino acid prepared in this way is covered with 200 cc. fresh acetyl chloride in a shaking flask, cooled in ice water, and 31 grams of freshly and rapidly pulverized phosphorus pentachloride added in two portions, with vigorous shaking, the fine powder is transformed to a crystalline product distributed throughout the liquid. After being shaken for about twenty minutes at 0°, it is shaken on the machine at room temperature for one hour, 3 grams more of phosphorus pentachloride added, and shaken for four hours longer. The solid is filtered off by means of his apparatus described under the heading "Filtration," washed with acetyl chloride, then several times with dry petroleum ether, and dried over phosphorus pentoxide in a vacuum. The product contained no phosphorus. Alanine (aminopropionic acid) derived from silk, behaved exactly like glycocoll.

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[1] Scholl, Roland, *Ber.*, **32**. 3494 (1899).

[2] Rinck, M., and Kossel, A., *Z. physiol. Ch.*, **33**, 5 (1901).

[3] Fischer, E., *Ber.*, **38**, 2915 (1905).

STIRRING AND SHAKING

Direct reference has been made under the heading "Solvents and Diluents," to the fact that materials interact best if dissolved in the proper proportions in a common solvent, in case they form too vigorous a reaction mixture in the absence of a solvent, either when simply mixed or when melted together. These favorable conditions cannot be achieved in many cases because of the lack of a suitable common solvent as, for instance, when nitrating and sulfonating materials insoluble in nitric or sulfuric acid. Under these conditions, the complete mutual contact provided by a solvent, must be replaced by mixing the constituents of the reaction mixture as intimately as possible by mechanical aids, *i.e.*, stirring or shaking must suffice. Excellent results may be obtained in this way, as instanced by the brilliant technical successes in this field, which greatly excel the laboratory because of better mechanical equipment. That stirring is highly essential to many chemical reactions is expressed in many factories by the saying "Nothing without stirring."[4] Since it has been recognized that shaking and stirring by hand are not sufficient, suitable apparatus has been constructed even for laboratory use, but it is not used as often as it should be, even though it is very convenient because mechanically driven. The excellent hot air motors which are set in motion by simply lighting a gas flame may be used. One of these, driving a shaking machine, will be shown later (fig. 152). Turbines or motors run by water or electricity are also available.

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[4] Hugel, E., *Ch. Zt.*, **45**, 199 (1921).

According to Hart,[5] the formation of tar in the ordinary method of preparing ortho- and para-nitrophenol may be avoided, and the yield of the para compound raised to 18 per cent, if the acid is well stirred while adding the phenol. A solution of 80 grams $NaNO_3$ and 100 grams concentrated H_2SO_4 in 200 cc. water is well stirred by means of a motor at 25°, and a solution of 50 grams crystalline phenol in 5 cc. alcohol is added, drop by drop. After the addition is finished, the stirring is continued for thirty minutes longer, the system allowed to stand for 1 hour and then worked up to the usual way.

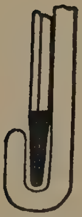

FIG. 145. STIRRING THERMOMETER (SCHOLZ)

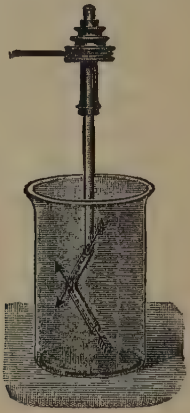

FIG. 146. STIRRER (FRANKENSTEIN)

Stirring

Thermometers are frequently broken when used as stirring rods in reactions in which liquids have to be mixed with each other, or with pulverized solids, if the temperature must be constantly observed. The bare thermometers are broken by striking against the walls of the container, even though the glass at the lower end of the mercury bulb is thickened. Scholz[6] has overcome this difficulty in the following practical way. He bends a glass rod as shown in figure 145, and fastens it to the thermometer with two rubber rings so that the thermometer cannot touch the walls of the vessel.

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[5] Hart, R., *J. Am. Ch. Soc.*, **32**, 1105 (1910).

Frankenstein[7] has recommended the following very efficient stirrer which is easily made and which has received lasting approval.[8] It consists of a glass rod of medium thickness with one end bent as shown in figure 146. There are two holes about the size of a pea at each bend. It is connected with a motor-driven glass rod, by means of a piece of rubber tubing. The rod gives the tube the necessary firmness. The action of this hollow stirrer on two immiscible liquids, for instance, is so great that droplets of a mixture of the upper, lighter, and of the lower, heavier liquid, are thrown out of the middle opening by the centrifugal force. Even as heavy a material

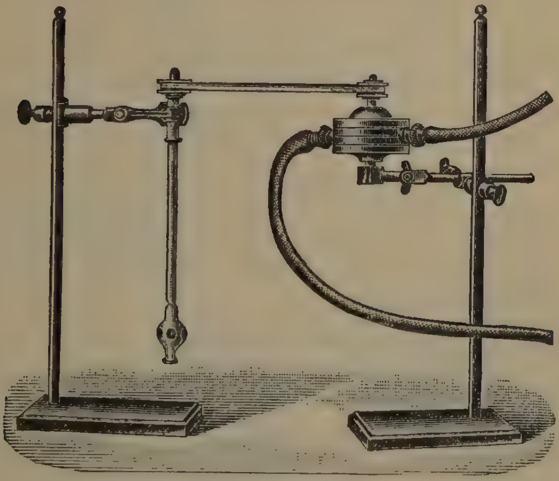

FIG. 147. WITT STIRRER

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[6] Scholz, A., *Ch. Zt.*, **36**, 541 (1912).
[7] Frankenstein, A., *Ch. Zt.*, **20**, 630 (1896).
[8] Thiele, J., and Straus, F., *Ann.*, **319**, 216 (1901).

as fine sea sand can be kept suspended indefinitely in water, and organic materials of all kinds still more easily.

Witt's[9] stirrer (fig. 147) consists of a small glass pear, 20 to 25 mm. in diameter, whose thick end is sealed to a glass rod, while the thin open end is turned downward. Around its greatest diameter the pear has four holes, each one as large as that at the open end. The glass rod passes through a closely fitting glass tube, 6 to 7 cm. long, which serves as a guide, and the upper end of the rod fits into a wooden pulley of such a size that a speed of about 5000 r.p.m. may be attained by direct connection with a Rabe turbine. Witt[10] later found that this centrifugal stirrer was faulty in that the glass rod serving as the shaft sometimes jams in the glass tube and breaks off. This may be remedied if a somewhat wider glass tube is used, and the rod wound with a tight spiral of thin aluminium wire. The soft aluminium acts as does the bearing metal of an iron machine axle, and at the same time, holds the lubricating oil between the coils of the spiral. The pulley is fastened more securely by a pin of hard wood driven into a slot in it. When this apparatus rotates in a liquid, the liquid is thrown out of the inside of the pear through the side opening by the centrifugal action; a vacuum is formed in the pear, causing the liquid to rise from the lower part of the vessel into the pear; but it is immediately thrown out and new quantities of liquid rise to replace it. This action may be easily observed if the apparatus is used to stir a heavy dark liquid, like a solution of iodine in carbon bisulfide, into a lighter one like water. The apparatus works very rapidly and powerfully, and if set up properly, a rotation of the whole liquid mass never occurs, and consequently, the container may be filled almost to the top without danger of overflow. Since the apparatus is so narrow, it may be inserted into flasks, and the glass tube serving as a bearing may be simply put into a cork. Thus, it is possible to thoroughly stir liquids boiling under a reflux or being distilled, etc., which is a great advantage at times. A liquid may be atomized to a fine mist if only the tip of the apparatus is immersed in it, or finally the apparatus may be used to aerate liquids if a thermometer tube is used as a shaft in place of the glass rod, and air or any other desired gas passed through its opening. Witt has found a mixture of vaseline and anhydrous lanolin to be the best lubricant for the bearing of the apparatus. The bearing runs hot and is ground down if not properly lubricated.

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[9] Witt, Otto N., *Ber.*, **26**, 1696 (1893).

[10] Witt, Otto N., *Ber.*, **48**, 751 (1915).

After years of daily experience in a factory laboratory with kettles provided with a stirrer and designed for high and low temperatures, as well as for vacuum distillation, Schwalbe[11] devised a kettle with a working space of 250 cc., which permits 50 to 100 cc. of liquid to be conveniently worked up with continuous uniform stirring (fig. 148).

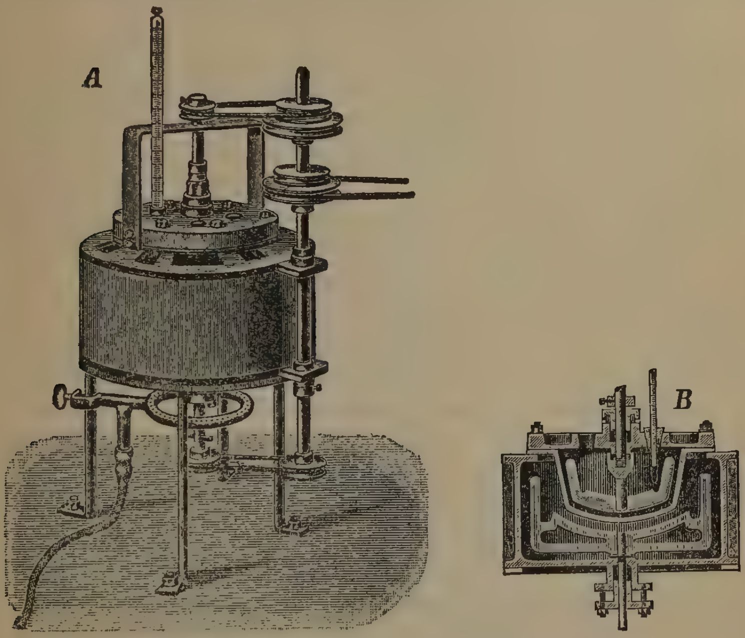

FIG. 148. STIRRING KETTLE (SCHWALBE)
a, external view; *b*, sectional view

He made the kettle cylindrical, keeping in mind the maximum cooling and heating surface, since a kettle of this shape permits much better stirring and also more rapid mixing of added solids or liquids than does a spherical one. It has the further essential advantage that there is very little space for the vapor to rise during vacuum distillations. The stirrer is of the simple wing type. A comparatively low rate of revolution is sufficient to raise the liquid up the walls of the vessel, and if the kettle is not too full, the constant return spreads the contents over the cooling or heating surfaces in a rather thin layer. If the stirring action is not sufficient for two immiscible liquids, it may be increased by introducing baffles fastened in the openings of the cover, or by increasing the rate of revolution. The axle has a ring shaped vessel cast to it, which prevents lubricating oil coming from the stuffing box of the stirrer, from entering the kettle, and protects the stuffing box from the action of corrosive vapors or corrosive liquids during vigorous stirring. Since the cover fits the edge of the stuffing box by means of a corresponding extension which grasps the ring shaped bowl, if the latter is filled with mercury, sulfuric acid, paraffin oil, etc., it is impossible for atmospheric air and moisture to enter through the stuffing box. The blades of the stirrer are made with a depression in their sides and these permit the immersion of a thermometer when the kettle contains as little as 50 to 100 cc. of liquid. The cover has three openings, one used for charging, the second for the reflux condenser, and the third for the thermometer. It has a layer of insulation about 1 cm. thick, which reduces as much as possible, unnecessary condensation during distillations, and undesirable heating during experiments at low temperatures. The vessel may be made perfectly tight by means of the sealing surfaces 3 cm. wide, which are fastened down by six powerful screws, using a luting material chosen according to the contents of the kettle (rubber with fabric lining, asbestos, pasteboard soaked with linseed oil or red lead cement). If the apparatus is made of an acid resistant casting, the luting material which is to make it air tight may be pressed in still more easily if the sealing surfaces are ground off, and a few narrow channels are provided; but even when enameled—the inside of the cover also is enameled—a vacuum of 20 to 30 mm. mercury may be attained. In this kettle it is possible, consequently, to carry on a vacuum distillation accompanied by stirring. However, according to Schwalbe, the vacuum distillation often suffers from the unavoidable bumping of the boiling liquid, and its foaming over cannot be avoided by either capillaries or fragments of porous solids, etc., in case it is not feasible to pass air through the contents of the kettle.

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[11] Schwalbe, C., *Ch. Zt.*, **29**, 670 (1905).

The kettle is designed for indirect heating and for direct cooling. For this reason, it is fitted into a larger jacketing kettle which is protected against cooling by insulation on its vertical walls. When working at low temperatures, the bottom of the jacketing kettle is also insulated by sheets of asbestos. As a consequence, the consumption of cooling mixture is very moderate, especially since the outer vessel has been fitted with a power stirrer acting from below. It is too seldom taken into account that the full cooling action is not developed until the quiet layers of the warmer liquid formed are continually disturbed by vigorous and constant stirring of the cooling mixture. In this way, it is possible to successfully carry on nitrations even in an enameled kettle filled to capacity at temperatures of -12 to $-15°$, using an ice-salt mixture as the cooling agent; certainly an admirable accomplishment, considering the poor heat conductivity of enameled iron. The advantages of external insulation and of the stirrer are also apparent when the outer kettle is used as a heating bath (water or oil, for example). If the heating bath is stirred it is unnecessary to superheat the bath, and consequently, the vapor of the distilling liquid much above the boiling point; a very slight interval between the temperature of the bath and the boiling point is sufficient. The kettle is heated by a movable ring burner clamped to the stand.

Both stirrers may be driven from a common vertical shaft placed on one side or still better, in case a horizontal transmission shaft is provided, each stirrer may be driven by a corresponding separate pulley connected with this shaft. If the cooling mixture is not prepared with ground ice, but with chunks of ice, the stirrer in the outer vessel may be stopped by them; and the shaft is fitted with a handle or a hand wheel for crushing the obstacle should this occur.

Mixtures boiling under a reflux may be stirred as described below. After Mermod and Simonis[12] found that the yields in many magnesium condensations (Grignard reaction) might be raised as much as 50 per cent by thorough stirring, they devised the apparatus shown in figure 149, which may be used extensively. The two ends of the bulb condenser *A* are just wide enough so that the stirrer, driven by the turbine *B*, may pass through. The vapors from the boiling liquid enter the inside of the condenser through the side opening *C*. In the special case being discussed, after the reaction is over, the necessary ice cold water is added through the side arm *D* of the condenser.

Süchting[13] has described a stirrer for glass vacuum apparatus.

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[12] Mermod, E., and Simonis, H., *Ber.*, **39**, 898 (1906).

[13] Süchting, H., *Z. anal. Ch.*, **47**, 755 (1908).

Figure 150 shows a wing stirrer with movable blades, which Brühl[14] considers particularly suited to flasks.

Shaking

The shaking of sealed tubes was described when they were discussed. Mechanical shaking is ordinarily used for one of two reasons. It either replaces hand shaking of separatory funnels, or it is used when reaction mixtures of any kind are to be shaken continuously during the reaction. In the first case, which is intended for working in the cold only, the separation of liquids which have been shaken together, must be finally accomplished in a separatory funnel to which they have been transferred. Figures 151 and 152 show shaking machines driven with water or hot air motors. Figure 152 shows

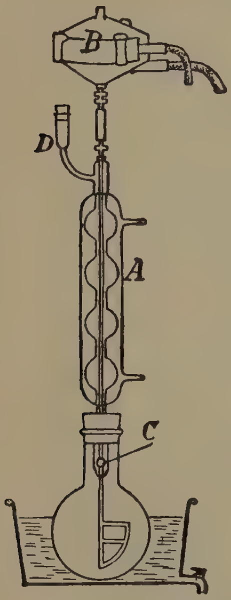

FIG. 149. STIRRING APPARATUS (MERMOD AND SIMONIS)

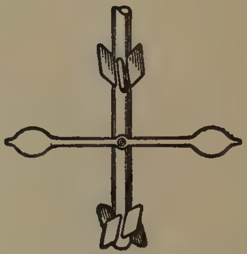

FIG. 150. PROPELLER STIRRER (BRÜHL)

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[14] Brühl, J. W., *Ber.*, **37**, 923 (1904).

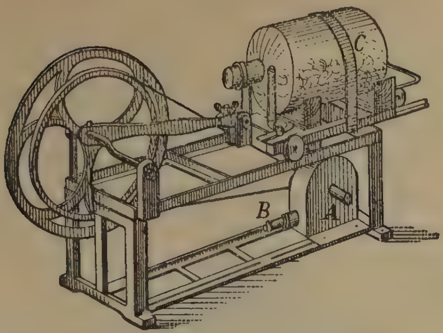

FIG. 151. SHAKING MACHINE WITH WATER MOTOR

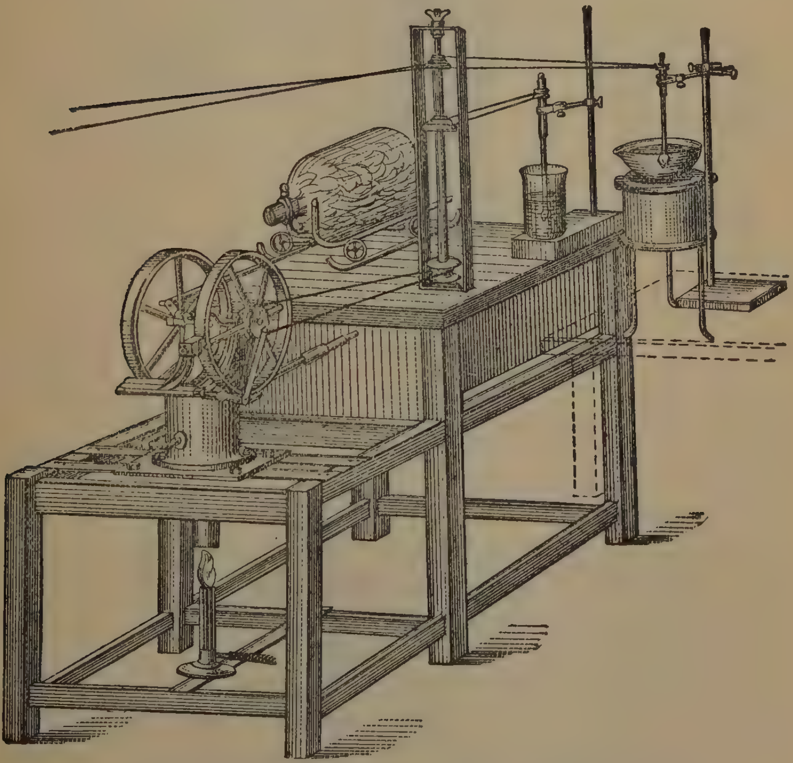

FIG. 152. SHAKING MACHINE WITH HOT AIR MOTOR DRIVE

how the motor, which can shake bottles containing as much as 6 liters of liquid, may be used for several purposes at one time.

Brühl[15] solved the problem of continuously shaking reaction mixtures while they are being heated. He designed this device particularly for metallo-organic syntheses. It was often necessary to prevent the zinc or sodium dust, or the powdered magnesium, from balling together and conglomerating with the solid reaction-products, since this causes unpleasant bumping and makes completion of the reaction impossible. It was, therefore, necessary to provide for continuous mixing of the ingredients during the reaction. None of the shaking and stirring apparatus then known served his purpose, because the reagents had to be thoroughly mixed while being boiled in ether, or other, even high boiling solvents, during the gradual addition of other reagents. That is, he had to use glass flasks fitted

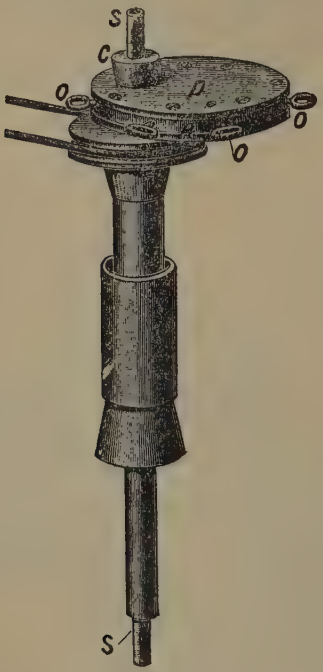

Fig. 153. Head Piece of Shaking Apparatus (Brühl)

with reflux condensers so that the course of the reaction could be observed.

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[15] Brühl, J. W., *Ber.*, **37**, 918 (1904).

The upper part of the apparatus (fig. 153) consists of a flat drum shaped brass box open below and closed above by a cover *D*, which can be screwed on. This hollow body is surrounded by a brass ring *R* sliding in a groove and carrying eyes, *o*, which are screwed and brazed in. The box is bored through eccentrically and tightly connected with a hard wood pulley *H*, which has a hole through the center. The shaft of the apparatus, a smooth brass rod or tube *SS*, passes through the common opening and is fastened by a rubber stopper *C*. Figure 154 shows a cross section of the eccentric and pulley (actual size). It can be seen that the wood of the pulley is continued above as a collar, *h*, which increases the stability of the connection with the eccentric and also provides the necessary friction surface for fastening the shaft by the rubber stopper.

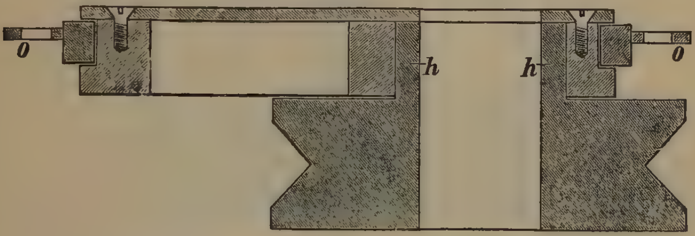

FIG. 154. SECTION OF SHAKING APPARATUS

Natural size

The apparatus may be used for shaking either a single vessel or several simultaneously, by using one or more of the lugs of the eccentric. Six flasks, whose capacities may be as much as one liter each, may be vigorously shaken at one time, and the results, according to Brühl, are astonishing.

He discusses the suspension of the reaction vessels as follows: He uses round bottom flasks connected by a soft cork (not rubber) with a vertical Liebig condenser 60 to 70 cm. long, which is clamped only at the upper end to the rod of a stand about 1 meter high. In this way, the flasks are arranged in an excellent radiating position which insures proper working of the apparatus. A simple cork connection between the reaction flask and the condenser is not sufficient, because the vigorous movements of the flasks would soon loosen them.

The flasks must be pressed elastically onto the corks and this is done by winding a cord around the neck of the flask and tying the ends over the water exit tube of the condenser jacket. The cork is coated with collodion to make it absolutely air and water tight. The reaction flasks are heated in an air bath through saucer shaped or spherical metal dishes placed under them.

According to Kempf[16] there was no apparatus which conveniently made it possible to agitate a reaction mixture vigorously and continuously while maintaining a desired temperature in the reaction vessel, (at least between 0° and 100°), and to collect any gas evolved during the reaction. The apparatus illustrated in figure 155 fills this need. It is made of glass, holds about 0.5 liter of liquid and is placed in a felt covered cabinet fastened on a shaking machine. The reaction mixture is fed in through the tower which may be connected with suitable gas measuring devices. The bulb-like extension completely prevents any of the liquid from spurting out, even when shaken most vigorously. It is easy to maintain any desired temperatures during the reactions by passing cold or hot water, steam, or a salt solution cooled below 0°, through the coil. The moving liquids are finely divided because of the resistance offered to their motion by the coil. For instance, a mixture of benzene and water was immediately beaten to a fine homogeneous emulsion.

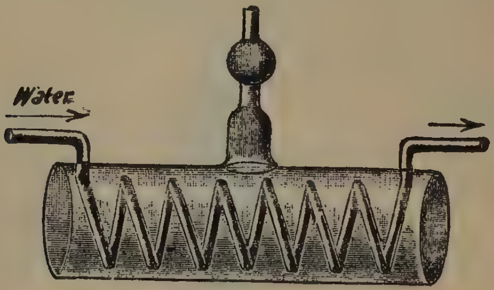

FIG. 155. SHAKING APPARATUS WITH INTERNAL TEMPERATURE CONTROL AND GAS OUTLET (KEMPF)

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[16] Kempf, R., *Ch. Zt.*, 30, 475 (1906).

CHAPTER XVI

MELTING POINT DETERMINATIONS

Landolt[1] made the first extensive investigations of the methods of determining melting points. These studies dealt with: (1) Melting and solidification of larger quantities with the thermometer directly immersed: (2) Heating of the substance in capillary tubes of various forms, including Piccard tubes[2] in liquid or air baths; (3) The Löwe method,[3] in which a platinum wire covered with the substance is heated in a mercury bath until melting produces contact of the metals and closes an electric circuit.

Landolt's results were as follows: The method of fusion and of solidification always gives results which agree very closely. He believes it to be the only method leading to sure results. However, it requires about 20 grams of the material. If larger quantities are used, the temperature of solidification is, in general, more easily determined than the temperature of fusion.

Melting points determined in capillary tubes of different forms may disagree considerably. Occasionally they agree with the true values, but the results obtained are usually too high, especially when narrow tubes are used. According to Landolt, the electrical method also yields results which do not agree very well, and tend to be too high.

Wegscheider[4] discusses this question as follows: In many laboratories there is a tendency to work for the "sharpest" possible melting point, even though the experiment can yield no sharp melting point. A sharp melting point is practically never observed in the ordinary method of using a capillary tube, because what is observed is a

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[1] Landolt, H., *Z. ph. Ch.*, **4**, 357 (1889).

[2] Piccard, J., *Ber.*, **8**, 687 (1875).

[3] Löwe, J., *Z. anal. Ch.*, **11**, 211 (1872); Christomanos, A. C., *Ber.*, **23**, 1093 (1890); Wolff, C., *Dingl. Polyt. Jour.*, **217**, 411 (1876); Himley, C., *Dingl. Polyt. Jour.*, **220**, 529 (1876).

[4] Wegscheider, R., *Ch. Zt.*, **29**, 1224 (1905).

"melting range," *i.e.*, the thermometer shows a higher temperature at the instant the substance is completely melted than when the first liquefied portion is seen. As to the tendency mentioned above, Meyer[5] states that the temperature at which the substance appears perfectly clear and transparent, after the meniscus is formed, should be considered the "melting point." This same tendency causes Reissert[6] to make the statement: "The point at which melting begins should always be observed." He bases this on the fact that the substance in the interior of the capillary is at a lower temperature than the outer glass wall. In general neither statement is justified, and accordingly, very extensive consideration of the determination of the melting point is given below.

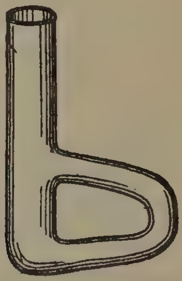

FIG. 156. APPARATUS FOR THE DETERMINATION OF MELTING POINT (THIELE)

DETERMINATION IN A CAPILLARY TUBE CLOSED AT ONE END AND PLACED IN A DOUBLE BATH

It is customary, in the laboratory, to determine melting points in capillary tubes, because minimum quantities of substance then suffice.

The material may be heated in the apparatus described by Thiele (fig. 156). It consists of a tube about 2 cm. wide and 12 cm. long, having an arm 1 cm. wide, bent so that it connects the lower end of the tube with the middle of it. Enough sulfuric acid is put into it, so that the upper opening of the bend is just covered when the thermometer bulb is placed about half way between the arms of the bend. When the bend of the side arm is heated, the sulfuric acid begins to circulate like the water in a hot water heating system; moving downward in the tube and causing a very uniform rise of the thermometer. This apparatus works much more evenly than any of the types without mechanical stirrers. It heats very rapidly, lags little, cools off very quickly, and is not more fragile than any other apparatus designed for the determination of melting points. The dust of the material adhering to the upper part of the capillary melts first when the heating is rapid, because the temperature of the acid falls as it flows downward in the tube, so that it is easy to tell when the melting point is being approached.[7]

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[5] Meyer, Hans, *Analyse und Konstitutionsermittelung organischer Verbindungen*, Berlin 3rd rvd, p. 101 (1916).

[6] Reissert, Arnold, *Ber.*, **23**, 2241 (1890).

There is no need of a special connection for fastening the capillary tube to the thermometer, if the bulb is moistened with a little sulfuric acid, and the capillary tube then drawn through this very small drop, moving it at the same time farther along the thermometer. The cohesion of the acid is sufficient to hold the capillary tube to the thermometer, even though there is no acid beyond the point where the capillary has been held with the fingers. The thermometer with the adhering tube can now be immersed in the acid in the test tube without danger of the capillary tube falling off; when cool enough after the determination is finished, they may be lifted out together.[8]

Friedrichs[9] has modified the melting point apparatus by making the front and back walls straight, so that a magnifying glass may be used when taking the reading. The errors due to the lag of the thermometer are avoided in this apparatus (fig. 157) by surrounding the bulb of the thermometer and the sample with a second vessel. The melting point tubes are introduced through the side arms, which obviates removing the thermometer. The sulfuric acid circulates in this case also, if the heating is not axial but tangential to the circular long section of the flask.[10]

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[7] Modifications of Thiele's melting point apparatus have appeared and offer certain advantages over the original design. Dennis, *J. Ind. Eng. Chem.*, **12**, 366 (1920); Bell, *Ind., Eng. Chem.*, **15**, 375 (1923).—R. A.

[8] In most cases this arrangement for holding the capillary tube to the thermometer is satisfactory. Where high melting compounds are involved, the acid bath loses its viscosity and the capillary tube sometimes slips off. A device attached to a thermometer to hold the capillary tube has been described. Köhler, *Z. angew. Chem.*, **27**, I, 528 (1914).—R. A.

[9] Friedrichs, F., *Z. f. angew. Ch.*, **34**, 61 (1921).

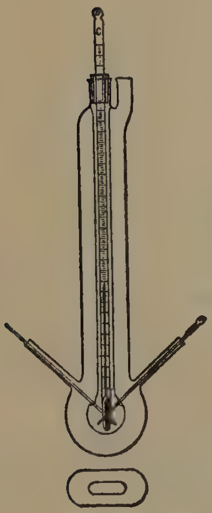

FIG. 157. APPARATUS FOR DETERMINING THE MELTING POINT (FRIEDRICHS)

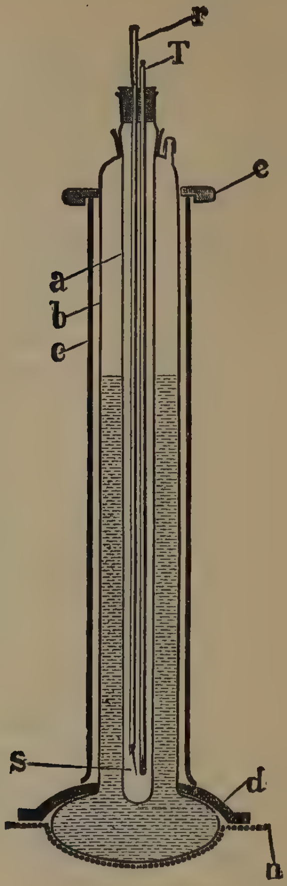

FIG. 158. LANDSIEDL'S APPARATUS

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[10] Although the Thiele apparatus is used almost exclusively to any other in Germany, the writer has never been able to appreciate any distinct advantage of this apparatus over the use of a small beaker as a bath with a tiny mechanical stirrer to keep a constant temperature. The circulation system of the liquid in the Thiele apparatus is not very efficient.

A small flask may be used as a bath into the bulb of which is sealed a small side tube through which the capillary and thermometer may be inserted. Mechanical stirring is easily accomplished through the neck of the flask. Kubota and Sakurai, *C. A.*, 19, 2147 (1925).—R. A.

Landsiedl's[11] apparatus (fig. 158) in which he claims that corrected melting points may be determined directly, will be discussed next. The tube, *a*, closed below, holds both the thermometer and the capillary tube, and serves as an air bath. It fits, by means of a ground glass joint, into the flask, *b*, which is filled with sulfuric acid to two-thirds its height. *b* is lens-shaped so as to offer the largest possible heating surface. An exit for the expanding air is in the ground joint, or next to it. The sample to be tested is introduced by means of the tube, *r*, whose lower opening is somewhat constricted so that the conical capillary tube, *s*, will remain hanging by its upper end when it is dropped down *r*. The tube, *r*, of this apparatus makes it possible to introduce the material whose melting point is to be determined, next to the thermometer, after the latter has already been heated almost to this temperature. About half of the bulb of the flask is embedded in a narrow-meshed stout wire gauze, *n*. Its upper half is covered with an asbestos shield, *d*, on which rests the glass cylinder, *c*, which served as a further insulator, and is closed at

TABLE 9

Effect of excellent insulation

TEMPERATURE	PERIOD OF HEATING	
	Apparatus without cylinder *c* and without asbestos cover, *d*	Apparatus with cylinder *c* and with asbestos cover *d*
°*C.*		
25		
100	4½	5½
150	7½	10
200	13	15
225	18	18
240	23	20
250	32½	22
254	40	22½
260	Thermometer reading varied from 254° downward and did not exceed 255° even during twenty minutes further heating	24
270		26
280		28½
290		32
300		36½
310		43½

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[11] Landsiedl, A., *Ch. Zt.*, **29**, 765 (1905).

the top by a cover, *e*. The figures in table 9 show the effect of this excellent insulation.

Of course there is no reason for not adding potassium sulfate to the sulfuric acid (see below), and thus make higher temperatures available.

A much more complicated, but very excellent apparatus for determining melting points has been devised by Stoltzenberg.[12]

The double bath may also be used for determining very low melting points. According to Krafft,[13] melting points as low as −60° may be determined by fastening sealed capillary tubes charged with the substance, to an alcohol thermometer in the usual way, and placing them in an air tight vessel containing liquid sulfur dioxide. If the latter is drawn off through a side tube by an air pump, the temperature falls very rapidly. It is well to include in the apparatus a manometer for reading the diminished pressure, for approximately fixing the thermometer. The whole apparatus is placed in a large cylinder containing a few drops of alcohol because otherwise, the apparatus if left in the air would become covered with a crust of frost, making it impossible to read the temperature.[14]

Kutscher and Otori[15] made use of the insensitivity of quartz glass, and did not employ, as did Graebe, a double sulfuric acid bath, but a double air bath which also permitted determination of the explosion point. For this purpose, a well fitting test tube of ordinary glass was placed in a small, long necked quartz flask, so that it closed end was about 1 cm. from the bottom of the flask. The thermometer, with a sample fastened to its bulb by a platinum wire, was put in the test tube in the ordinary way. No special heating liquid was used, but the sample was surrounded only by the double air jacket. The outer quartz flask, because of its nature, could either be heated directly, or an asbestos plate was placed between it and the flame. This apparatus may also be used to determine the explosion point. The explosive material is placed in wide, conical melting tubes which are fastened directly to the thermometer bulb. Explosion or flashing may take place in a melting tube of this form, without damaging the apparatus.[16]

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[12] Stoltzenberg, H., *Ber.*, **42**, 4322 (1909).

[13] Krafft, F., *Ber.*, **15**, 1694 (1882).

[14] For melting points at low or high temperatures in a nontransparent bath an ingenius device has been described which allows a pointed rod to rest on the ring of the solid substance and to observe the sinking point of the rod. Stock, *Ber*,, **50**, 156 (1917).

Other types of melting point apparatus have been described which should be considered by one interested in getting the most convenient form. Hibbert and Thompson, *Analyst*, **43**, 216 (1918); Mytenbogaart, *Chem. Ztg.*, **46**, 493 (1922); Washburn, *Ind. Eng. Chem.*, **16**, 854 (1924); Mason, *Chem. and Ind*, **44**, 577 (1925).—R. A.

[15] Kutscher, F., and Otori, J., *Z. physiol. Ch.*, **42**, 193 (1904).

DETERMINATION IN CAPILLARY TUBES OPEN AT BOTH ENDS

Capillary tubes open at both ends are used especially for determining the melting points of fats and solid fatty acids. They are also employed for determining the softening points of all kinds of materials.

They were recommended for the first purpose long ago by Bouis.[17] The capillary tube open at both ends, is plunged about 5 mm. in the melted fat and the fat allowed to solidify in the tube, which is then fastened to the thermometer by a rubber ring. The water of the bath is heated, and the temperature recorded at which the water in the inner test tube of the Graebe apparatus rises along with the melted fat in the capillary tube. This method has been used very frequently by the writer and gives very reliable results with stearic and palmitic acids, or with mixtures of them.

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[16] Very popular in the French laboratories is the Maquenne block for determining melting points. It is particularly useful for substances of high melting point (up to 400°) and for substances tending to decompose before reaching the melting point. The apparatus may be purchased from many French concerns such as Poulenc Frerés.

An automatic device for determining melting points which involves the principle of completing an electric circuit at the melting point of the substance has been described. Dubosc, *Rev. prod. chim.*, **28**, 115 (1925).

This has been improved by a slight modification. MacMullin, *J. A. C. S.*, **48**, 439 (1926). And still further improved even more recently. Palmer and Wallace, *J. A. C. S.*, **48**, 2230 (1926).

The writer has seen the apparatus in use and can recommend it particularly for any one with many melting points to determine.

Melting points of substances which are available in very small amounts can be made in a micro melting point apparatus. It is a useful addition to laboratory equipment. Clevenger, *Ind. Eng. Chem.*, **16**, 854 (1924).—R. A.

[17] Bouis, J., *Ann. Chim. phys.*, [3], **44**, 152 (1855).

Krämer and Sarnow[18] use a somewhat similar method for determining the melting or rather the softening point of asphalt, pitches and like materials. Twenty-five grams of the asphalt, etc., is melted at 150° in a small beaker in an oil bath. The layer of molten asphalt should be about 1 cm. thick. A glass tube about 10 cm. long, 6 to 7 mm. in diameter, and open at both ends is plunged into this. The upper end is closed with the finger when the tube is withdrawn. It is allowed to cool in a vertical position in the air. The asphalt sticking to the outside is then removed with the fingers. The asphalt layer in the tube is now about 5 mm. high, and about 5 grams of mercury is poured on it from a graduated tube. The melting point tube is then placed in a beaker filled with saturated brine, and the beaker suspended in a second one filled with clear paraffin oil. A thermometer is placed next to the melting tube so that the bulb is opposite the asphalt layer. The temperature at which the mercury breaks through the asphalt layer is recorded as the melting or softening point of the asphalt. According to Wendriner,[19] determinations of different analysts using this method may disagree as much as 5°. He, therefore, recommends that the sample of asphalt be placed in a tube whose ends are ground evenly, and that the rod of solidifying asphalt be made exactly 10 mm. long by inserting a plane-ground glass rod; the differences in melting point are then less than 1°. Salt water no longer suffices for the heating bath for high melting pitches, wood pitch 205°, for example, so rather wide melting tubes closed at the bottom with a cork, should be used and enough pitch added so that when melted, it forms a column about 5 mm. high in them. After the pitch has solidified, the cork is removed and the determination carried out directly in molten paraffin, since the layer of air trapped between the pitch and the liquid paraffin when the tube is plunged into the paraffin, makes direct contact of the two substances impossible. Otherwise the pitch would dissolve in the liquid paraffin.

DETERMINATION IN CAPILLARY TUBES CLOSED AT BOTH ENDS

Long ago, Riban[20] determined the melting point of the addition-product of hydrochloric acid and a terpene, $C_{10}H_{16} \cdot HCl$, which easily gives off its hydrochloric acid, by using a capillary tube closed at both ends and filled with hydrogen chloride. Since chloranil sublimes completely before it melts, Graebe[21] placed a little of it in a capillary tube which he then sealed, and was then able to determine the melting point as 290°.

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[18] Krämer, G., and Sarnow, C., *Chem. Industrie*, **26**, 55 (1903).

[19] Wendriner, M., *Z. angew. Ch.*, **18**, 622 (1905).

[20] Riban, J., *Bull.*, [2], **24**, 14 (1875).

Later Michael,[22] as the need arose, further developed the use of tubes sealed at both ends, and so since 1895, it has been possible to determine the melting points of organic compounds, the melting points of some of which previously could not be determined at all. Some of these compounds, fumaric acid,[23] for instance, sublime before the requisite temperature is reached; others like dibromsuccinic acid[24] decompose before they melt; while the melting points of other products are so high, that the apparatus devised or in use at that time, was not suited for the determination. Since the lack of this extremely characteristic property often makes it necessary to resort to laborious analyses and studies of the decomposition of the material, he justly assumed that there would be much interest in a method eliminating the great majority of these exceptional cases. He proceeded from two standpoints; in the first place, it did not seem impossible that if the unstable or sublimable substance were brought into a liquid which already had been heated almost to the melting point in question, and then rapidly heated further, the decomposition or else the sublimation of the sample might be avoided; further it seemed probable that completely sealing the tube would have a similar effect, in that the substance could thus be subjected to a somewhat greater pressure.

When determining melting points under 300°, he used the apparatus shown in figure 159, which he had previously devised but now modified by having a narrow glass tube closed below, and bent at a right angle above, and which could easily be moved up and down through a second opening next to the thermometer. The glass projections (mentioned above) were fused about 30 to 40 mm. above the lower end of this plunger. A piece of platinum wire was fastened just above them and then loosely wound two or three times around the plunger, forming a spiral which serves to hold the melting point tube.

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[21] Graebe, C., *Ann.*, **263**, 19 (1891).

[22] Michael, Arthur, *Ber.*, **28**, 1629 (1895).

[23] Fittig, R., and Dorn, L., *Ann.*, **188**, 87 (1877).

[24] Kekule, Aug., *Ann.*, Supl. II, **90**, (1862); Hill, H. B., *Ber.*, **13**, 735 (1880).

Michael found ordinary melted paraffin to be the most practicable liquid for determining melting points lying between 300 to 400°. The more convenient materials for charging such baths, recommended by Scudder, are given later. According to Michael it is essential when making these determinations that uniform heating be maintained by using the stirrer. To avoid superheating, it is necessary to slip a thick asbestos cover, having a circular opening, over the heating tube almost to the level of the thermometer bulb.

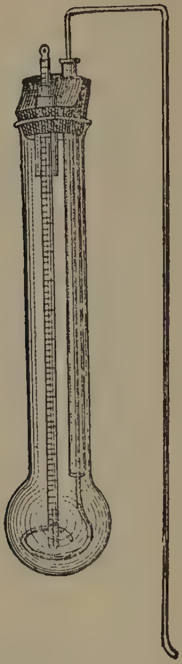

FIG. 159. MICHAEL'S APPARATUS

For experiments at temperatures of 400 to 450°, Michael used a metal bath in which the melting point apparatus was immersed so far that the melting point tube was just below the level of the metal. He satisfied himself that correct melting points could be obtained in a bath of this kind, provided the heat was well distributed. This was done by having the lower end of the stirrer wound in three coils, but it should be noted that a temperature of 450° could only be reached when the stirrer was moved continuously. However, under these conditions, it is difficult to accurately observe the instant of melting. This difficulty was eliminated by having a beam of sunlight reflected on the bulb of the thermometer. The melting point tube should be at least 1 mm. in diameter, since Michael found that the influence of capillarity on the melting point is, in general, greater in determinations in sealed tubes than Landolt[25] found in ordinary determinations. In using the plunger, it is well to also fasten a small tube to the thermometer in order to know when to immerse the plunger; but it is necessary to emphasize that the correct melting point can be determined only by several trials.

Fumaric acid when placed in an open tube and plunged into sulfuric acid heated to 280°, did not melt. If the liquid was rapidly heated, most of the fumaric acid sublimed below 290°, the slight residue melted at this temperature. The same behavior was observed when the tube was plunged into sulfuric acid heated to 290°. When heated from room temperature, in sealed tubes, dark spots appeared at about 260°, but complete fusion occurred at 286 to 287°. If a sealed tube was plunged into sulfuric acid heated to 282°, little of the material sublimed, and the rest melted at 287 to 288°.

Chloranilic acid, according to A. W. Hofmann,[26] begins to sublime at 150° and disappears rapidly at 210 to 220°; when heated rapidly, it melts with charring. The sublimation starts even in the water bath. When heated in the ordinary way, or even rapidly in either open or sealed tubes, most of it sublimes before the melting point is reached, but if it is fastened to the plunger and immersed at 278°, it melts at 283 to 284° in either open or sealed tubes; while, as stated above, Graebe found it melted at 290°.

The melting point of artificial indigo blue cannot be determined if it is gradually heated in open or in sealed tubes, because it decomposes. If enclosed in sealed tubes and immersed at 385°, it melts with decomposition to a purple red liquid at 390 to 392°.

The influence of sealing the tube on the behavior of materials such as fumaric acid, for example, when they are heated, is very remarkable, and Michael believes that the difference can scarcely be explained by the increased pressure produced and that special experiments should be made to determine the influence of pressure on the melting point of organic compounds so as to clear up this phenomenon. He points out that a considerable difference is observed with many organic materials, if the melting points are determined in closed instead of open tubes.

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[25] Landolt, H., *Z. ph. Ch.*, **4**, 371 (1889).

[26] Hofmann, A. W., *Ann.*, **52**, 59 (1844).

THE TRUE MELTING POINT

According to Reissert,[27] who as mentioned before has been particularly interested as to which temperature should be regarded as the true melting point, the temperature of incipient melting should be taken as the true melting point. Since the temperature within the capillary tube is always a little lower than on its walls, the particles adhering to the glass wall always melt a little sooner than the parts within and the liquefaction of these first portions lies nearest to the true melting temperature. Consequently, it is often advisable to empty the capillary, after it has been filled with the sample, and to determine the melting point of the particles which remain sticking to the glass.

The errors arising from inaccurate melting point determinations are illustrated by the conclusion drawn by Howe,[28] as late as 1895, that phthalic acid exists in two modifications, one melting at 203°, the other at 184°. On the basis of these findings, he wished to include in the literature an α- and a β-phthalic acid, because he assumed that in one case, the carbon atoms were bound to the carboxyls by single bonds and in the other by double bonds. Largely because of his melting point determinations, he reopened the question of the isomerism of 1,2− and 1,6− benzene derivatives which had been frequently discussed before, and finally decided in the negative, but as he thought, wrongly. However Graebe[29] investigated Howe's findings, and showed that there could be no question that phthalic acid does not give a definite melting point in the apparatus usually employed.[30] The melting may be made to take place between 180 and 200°, at will, depending on the method of heating, the size of the sample and the diameter of the melting point tube. As a rule, he found it to be 195°, somewhat lower when the bath was heated slowly, and somewhat higher when heated quickly. Perhaps the new method

[27] Reissert, Arnold, *Ber.*, **23**, 2241 (1890).
[28] Howe, W., *Am. Chem. J.*, **18**, 390 (1896).
[29] Graebe, C., *Ber.*, **29**, 2802 (1896).
[30] Graebe, C., *Ann.*, **238**, 321 (1887).

of Michael, which will be discussed at the end of the chapter, may even yield a reliable figure for the melting point of phthalic acid which so easily forms an anhydride. This example shows most plainly the interest attached to reliable melting point determinations and the great value of any improvement in methods.

GENERAL BEHAVIOR OF SUBSTANCES WHEN MELTED

Experience has shown that impurities practically always lower the melting point to a marked degree. A particularly striking example is given by Salkowski.[31] He found that a mixture of 35 parts of hydrocinnamic acid and 65 parts phenylacetic acid melts even at 21°, and remains liquid for a long time at room temperature, whereas pure hydrocinnamic acid melts at 77°, and pure phenylacetic acid at 47.5°.

A rise in melting point is only rarely encountered. Thus Wallach[32] mentions that impure samples of camphor derivatives melt higher than pure ones.

Whole classes of materials show definite behavior with reference to their melting points. Thus position isomers having almost the same melting points, usually differ considerably in the melting points of their acetyl derivatives and the melting points of the hydrazones[33] are only found to be constant when rapidly heated.

Particular difficulty is encountered in determining the melting points of materials prone to lose water. The experiences in connection with the melting point of camphoronic acid are cited as an example. Kachler[34] recorded it as 110° or 115°, and stated that it was difficult to determine. Kissling[35] found it to be 137°. Kachler and Spitzer[36] later found that the melting point could not be determined accurately. If the acid is placed in a thin walled tube and gradually heated in a sulfuric acid bath, it begins to melt between 135 and 140°, and if the solidified substance is reheated, it melts at a much lower temperature. To avoid the loss of water as much as possible, it should only be heated for a very short time before the actual melting. If the tube containing air-dried camphoronic acid is plunged into sulfuric acid at 140°, the material remains unchanged at first, and only melts when heated above 150°, to about 158°. If, however, the air-dried material is kept for some time at 100 to 120°, it is almost completely converted into the compound $C_9H_{12}O_5$, which melts constantly at 135 to 136°. Reyher[37] found that when heated rapidly, *i.e.*, if the tube is plunged first into an oil bath at about 120°, the acid begins to melt at 147° with loss of water, but the melting is finished at 151° with intumescence. On the other hand, if he heated very slowly with a small flame, the melting began at 139°, was quite definite at 139 to 141°, and at 141.5° the melting was over, with distension. According to Hess,[38] pure camphoronic acid, $C_9H_{14}O_6$, melts at 136 to 137° if the temperature is raised slowly above 100°, *i.e.*, only about 1° per minute, since most of it has already been converted into anhydrocamphoronic acid, $C_9H_{12}O_5$, by loss of water. However, if the melting point tube charged with fresh acid is plunged into a bath already at that temperature, considerable time elapses before the melting begins. If the bath is heated very rapidly, melting always occurs between 148 and 150°. Bredt[39] then found that camphoronic acid dried at 100°, melts at 136 to 137°. It may be seen from the data of various investigators, that the melting point of camphoronic acid varies with the rate at which the bath is heated. It also changes with the diameter of the melting point tube, since it melts sooner in a narrow tube than in a wide one, in accordance with Reissert's views. The loss of water which is more or less favored by the heating, is the chief cause of this behavior, since a mixture of the acid with its anhydride is being melted, rather than a uniform material. Similar phenomena have been observed with other acids of the camphor series,[40] and also with trimethylsuccinic acid,[41] etc.

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[31] Salkowski, H., *Ber.*, **18**, 321 (1885).
[32] Wallach, O., *Ber.*, **25**, 919 (1892).
[33] Fehrlin, H. C., *Ber.*, **23**, 1583 (1890).
[34] Kachler, J., *Ann.*, **159**, 288 (1871).
[35] Kissling, Dissert., Würzburg, 1878.
[36] Kachler, J., and Spitzer, F., *Monatsh.*, **6**, 176 (1885).

That in many cases the water content is certainly the cause of the behavior when melting, follows from Woffenstein's[42] study of the platinum double salt of conine hydrochloride, which crystallizes with one molecule of water, $(C_8H_{17}N \cdot HCl)_2PtCl_4+H_2O$. The hydrated salt melts at about 78° if it is suddenly brought into a melting point apparatus heated to this temperature. On the contrary, it does not melt below 175° if it is heated slowly in the melting point apparatus in the usual way, since the water is lost very easily. No matter how it is heated, the anhydrous salt shows no difference in melting point.

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[37] Reyher, R. G., Dissert., p. 41, Leipzig, 1891.

[38] Hess, Arnold, *Ber.*, **28**, 2687 (1895).

[39] Bredt, J., *Ann.*, **226**, 252 (1884).

[40] Tiemann, F., and Semmler, F., *Ber.*, **28**, 1351 (1895).

[41] Bredt, J., *Ann.*, **292**, 78 (1896); see also Auwers, K., and Oswald, S., *Ann.*, **285**, 304 (1895).

[42] Wolffenstein, Richard, *Ber.*, **27**, 2617 (1894).

Many materials also show so called double melting points, in that the temperature of incipient melting and of complete fusion lie far apart. *p*-Azophenetole[43] is an example. It melts constantly at 136° and forms a turbid liquid which only becomes clear and transparent at 165°. Such cases involve the formation of so called "liquid crystals," which were more closely studied first by Lehmann and Schenk,[44] and concerning which Lehmann[45] later wrote extensively.

Dibenzoylacetone[46] melts if plunged into a bath heated to 85 to 90°, becomes solid again around 93°, and melts for the second time at 101 to 102°.

MATERIALS FOR CHARGING BATHS

Double baths are usually filled with concentrated sulfuric acid. Although sulfuric acid boils at 338°, it is not suitable for melting point baths at temperatures far below this, because of the fumes given off. In 1903, Scudder[47] recommended making use of the fact that bisulfate does not begin to emit sulfuric acid vapors except at temperatures much higher than that given above, and this made it possible to determine melting points up to 360°, just as conveniently as those far below this limit could be found up to this time. For melting points up to 325°, he advises a mixture of 7 parts sulfuric acid (d.

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[43] Gattermann, L., and Ritschke, A., *Ber.*, **23**, 1742 (1890); Noelting, E., Grandmougin, E., and Michel, O., *Ber.*, **25**, 3332 (1892); see also Rotarski, Th., *Ber.*, **41**, 866 (1908); Vorländer, D., *Ber.*, **41**, 2033 (1908).

[44] Vorländer, D., *Ber.*, **40**, 1415 (1907); Claisen, L., and Smith, A., *Ann.*, **277**, 191 (1894); Schenk, R., *Krystallinische Flüssigkeiten*, Leipsic, 1905; Lehmann, O., *Flüssige Krystalle*, Leipsic 1904.

[45] Lehmann, O., *Z. angew. Ch.*, **19**, 1637 (1906); see also Lehmann, *Flüssige Krystalle und die Theorien des Lebens*, Leipzig, 1906.

[46] Claisen, L., *Ann.*, **291**, 74 (1896).

[47] Scudder, H., *J. A. C. S.*, **25**, 161 (1903).

1.84) and 3 parts potassium sulfate heated together for five minutes. This mixture remains transparent even at room temperature, and if discolored by dust, etc., which has fallen into it, it may be decolorized by adding a trace of potassium nitrate. A mixture of 6 parts of sulfuric acid and 4 parts potassium sulfate may be used for melting points between 325 and 360°. According to him, fused zinc chloride is the most suitable material for higher temperatures, up to 600°. It expands on cooling, and therefore, should be poured out of the container after the determination is finished, so as to avoid breakage. If has the further disadvantage that it soon becomes opaque and there is no simple method of restoring its transparency.

The use of water, paraffin, and metal-baths was mentioned above, and of course glycerine, olive oil, and similar materials[48] may be used (see also in the chapter on baths, the subheading "Oil and Metal Baths").

CORRECTED MELTING POINTS

According to Reissert,[49] the zero point of the thermometer used for these determinations should be determined from time to time, and the corresponding correction applied. Allowance for the exposed mercury column must always be made, since otherwise, differences of several degrees may be encountered because of the greatly varying errors of the thermometers. If the extensive Rimbach tables[50] are available, it is very simple to make the correction. According to Rimbach, Kopp's method of computing the correction (see the subheading "Thermometers" under "Distillation") gives too low values for long threads, and too high ones for short ones.

Ordinarily no importance is attached to such corrections, although they would be valuable in many cases. Roth,[51] who before Landsiedl designed an apparatus, based on the double baths described above, which was capable of giving rather exact figures without the application of corrections, discusses this question somewhat as follows: The melting points of a material given in a chemical publication refer, in general, to the uncorrected melting point. In most cases, the correction is neglected in spite of the fact that the value of the corrected figures would be greater both for the literature and the practical chemist. If the corrections were generally introduced, the frequent differences between the published and the observed figures would largely disappear. A sharp melting point may perhaps be the chief objective for determining the melting point of a new compound. However, if the melting point is to be used later, as an aid in identifying the compound, it is highly desirable, or indeed essential, that there be complete agreement between the melting point found and the one previously published.[52]

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[48] For temperatures between 150 and 350° by far the most convenient liquid is medicinal mineral oil.—H. T. C.

[49] Reissert, Arnold, *Ber.*, **23**, 2241 (1890).

[50] Rimbach, E., *Ber.*, **22**, 3072 (1889).

[51] Roth, C. F., *Ber.*, **19**, 1970 (1886).

The differences in the published uncorrected melting points are probably also increased because the determinations are not made under similar conditions. They are practically all determined with the scale of the thermometer outside the acid extending into the air, and with the bulb of the thermometer immersed sometimes higher, or sometimes lower in the sulfuric acid, which may be heated either directly or indirectly.

Roth devised the apparatus shown in figure 160 so that melting points might always be determined under the same conditions without making a correction each time. He hoped that its use would make it possible to read off a corrected melting point directly.

A glass tube *c*, 15 mm. wide extends to within 17 mm. of the bottom of the round flask *a*, which is 65 mm. in diameter, 200 mm. long, with a neck 28 mm. wide. The tube *c* is closed below, and is sealed into the neck *b*, of the flask at *g*. A tubulure 11 mm. wide is let in at *d*, and has a round opening on one side A hollow ground glass stopper which also has an opening at the side, fits in this tubulure. The flask *a* is filled with colorless concentrated sulfuric acid about as far as the mark *f*, through the tubulure, and the stopper *e* is then inserted so that the openings of *e* and *d* correspond. When the acid is heated it rises in *b*, and consequently a thermometer introduced in *c* will be in an air bath surrounded by hot sulfuric acid up to approximately the 280° mark.

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[52] Elimination of the necessity of making stem corrections is possible by the use of thermometers with stems already corrected for total immersion, 3-inch immersion and 1-inch immersion ranging from 0 to 400°. The actual readings are claimed to be accurate within 1° at 300°. The thermometers can be purchased at a nominal price from Hiergesell Brothers, Philadelphia.—R. A.

His next problem was to determine whether a uniform temperature prevailed in this air bath, or whether there were temperature differences at different levels. The latter is the case, but these differences were found to be very slight. When heating up (60 to 70°) there was a difference of 8°, which could be reduced to 3 to 4° by slower heating. At higher temperatures, an equilibrium was gradually established of itself, even with progressive heating, and at about 150°, the difference again was 3 to 4°; a further compensation of the temperatures does not occur. The correction occasioned by this difference in a melting point determination is 0.16°, an amount which may be neglected all the more because even the present methods of correct-

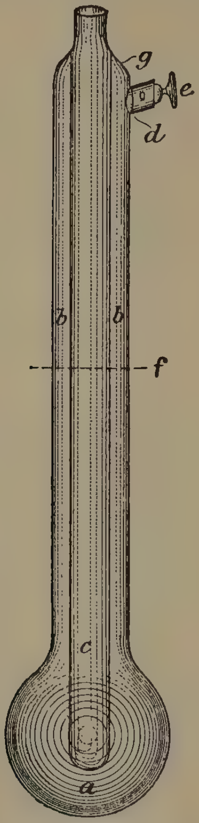

FIG. 160. ROTH'S APPARATUS

ing the melting point do not exclude equally large or even larger differences. According to this, the melting points read in the above apparatus must be the corrected ones; in fact, he showed experimentally that the melting points found agreed with those determined in open sulfuric acid and then corrected by an accepted formula,[53] as closely as the errors of observation permitted.

He used the same thermometer for all the determinations shown in table 10. For those in open sulfuric acid, he immersed it to the −10° mark on the scale, and in the determinations in the melting point apparatus, the thermometer was surrounded by sulfuric acid up to the 280° mark.

TABLE 10

Roth's melting point determinations

	AVERAGE TEMPERATURE	MELTING POINT		
		H_2SO_4	Apparatus	Corrected
	degrees	*degrees*	*degrees*	*degrees*
Benzoic acid...	35°	121.5	123	123.3
Urea	35	132	133.5–134	134.1
α-Picoline mercury double salt	35	154	156.5–157	157
Pyridine mercury double salt	40	174.5	178	178.4
β-Dinitro-naphthalene	35	168.5	172	172.2
Nicotinic acid	50	228	235	234.6

The apparatus has proved very valuable in practice. The sulfuric acid after having been in use for more than a year was still almost colorless and of practically the original density. It must be emphasized above all that the melting point determinations may be made very sharply in this apparatus, because overheating of the sulfuric acid does not occur easily, even though large flames must be used to attain higher temperatures. For one thing, the comparatively large quantity of acid in the apparatus hinders such overheating and, also, an extraordinarily vigorous exchange between the colder and warmer layers of the acid which likewise vigorously opposes such overheating is occasioned by the pressure exerted on *a* by the high columns in *b*.

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[53] $0.000156\ a\ (t - t_0)$. t = Boiling temperature. t_0 = Temperature of the exposed thread. a = Length of exposed thread in degrees. 0.000156 is the apparent coefficient of expansion of mercury in glass.

Roth stated that the only disadvantage of his apparatus was that it was difficult to attain temperatures above 250° in it, but this has been overcome by Scudder's recommendation to add potassium sulfate to the sulfuric acid.

If in concluding, the statments regarding melting point determinations are considered in sequence, it is apparent that these points may only be really determined in capillary tubes; that the value found is greatly dependent on the method used, because the procedure gives rise to differences depending even on the width of the capillary tube used. In short, if melting points are to be duplicated conveniently, it is best, whether using open or closed capillary tubes, to follow the procedure advocated by Reissert and recommended above, in which the capillary tube is charged, and then emptied, and the melting point of the residue adhering to the walls determined. This melting point will be independent of the diameter of the capillary. Any publication of the melting points should particularly state that they have been determined in this way.

CHAPTER XVII

DETERMINATION OF THE BOILING POINT OF SMALL QUANTITIES OF LIQUID

A. SIWOLOBOFF METHOD

Siwoloboff[1] recommends for this purpose, the following procedure by which the boiling point of even one drop of a pure compound may be determined. In this, he used, though certainly without intention an idea originated by Schumann[2] who wished to prevent the bumping of boiling liquids by means of the continuous escape of air bubbles from a capillary.

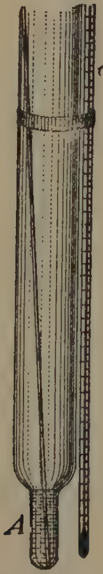

FIG. 161. SIWOLOBOFF'S APPARATUS

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[1] Siwoloboff, A., *Ber.*, **19**, 795 (1886).

[2] Schumann, Th., *Z. anal. Ch.*, **9**, 249 (1870); *Am. J. Pharm.*, **41**, 527 (1869).

The liquid to be tested is placed in a glass tube whose end has previously been drawn out and sealed. A capillary tube sealed at *A* (fig. 161), is then introduced into this, thus bringing a small bubble of air into the liquid. The glass tube prepared in this way, containing the liquid to be tested, is fastened to a thermometer and the whole is heated in a bath with stirring, as when determining the melting point.

Before the boiling point of the liquid under investigation is reached, several air bubbles escape from the capillary tube, as is usually the case when a liquid begins to boil. These rapidly become more numerous, and finally form a thread of small vapor bubbles. At this instant, the thermometer indicates exactly the boiling point of the liquid. The determination must be repeated several times and the mean taken.[3] The capillary prevents any delay in the boiling of the liquid, and a new one must be used for each experiment.[4]

Biltz[5] who recommends Siwoloboff's method very highly, found, when he used it in an attempt to determine the boiling point of a small quantity of tetrabromoethane, that this compound decomposed at atmospheric pressure. He, therefore, connected the test glass with a suction pump and a manometer, and easily succeeded in determining the boiling point of several drops of this material with sufficient accuracy. He found 144° at 41 mm. pressure, while it had been given as 139° for large quantities of the substance.[6]

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[3] A convenient modification of this method is described by Mulliken, *The Identification of Pure Organic Compounds*, vol. **1**, p. 222; John Wiley and Sons, New York, 1908. Mulliken recommends removing the flame when the boiling point has been exceeded and observing carefully the temperature at which "the liquid is seen to be about to recede into the capillary chamber. The temperature at the moment of recession is that at which the liquid remaining in the tube would begin to boil."—J. R. J.

[4] O'Dowd and Perkin (*Trans. Farad. Soc.*, **4**, 95 (1909) have devised a modification of the Siwoloboff apparatus and have carefully examined the modified procedure with a variety of organic liquids.—J. R. J.

[5] Biltz, Heinrich, *Ber.*, **30**, 1208 (1897).

[6] One of the oldest and simplest methods is that of Pawlewski (*Ber.*, **14**, 88 (1881)).

Bolduirev (*J. Russ. Phys. Chem. Soc.*, **48**, 1862 (1916); *Chem. Abs.*, **17**, 3444 (1923) describes a modification of the method of Pawlewski (*Ber.*, **14**, 88 (1881)) which is virtually a distillation of the substance from a small test-tube provided with a side-tube. This tube is fitted with a cork through which a thermometer passes and is wrapped with asbestos and fitted into an aperture

B. SCHLEIERMACHER'S METHOD

Siwoloboff's method answers for many though not all cases, since its results cannot be especially accurate. If accuracy is essential, Schleiermacher's method[7] may be used. The procedure is not difficult but is rather inconvenient. It may be applied to materials which are solid or liquid at ordinary temperature, and the boiling point may be determined with at least as great accuracy as given by the ordinary methods with larger quantities of liquid.

The procedure is essentially as follows: The sample is placed in the closed arm of the U-tube. This arm is then completely filled with mercury. The open arm is empty down to its lowest part, which is also filled with mercury and the thermometer is inserted in it. If the U-tube is heated in a liquid bath until vapor of the substance is evolved, the desired boiling point is obtained if the temperature is taken at the instant when the mercury levels in both arms are the same; the vapor is then exerting atmospheric pressure.

In order to make the U-tube, and to fill it with the material and mercury, without admitting air, a piece of dry, clean, ordinary bending tubing about 50 cm. long and 6 to 8 mm. wide, is drawn out at one end to a capillary (fig. 162) about 1 to 2 mm. wide (of course no water vapor must enter the tube). The capillary is drawn out again to a hair-like capillary about 50 mm. long at the place where it joins the wider tube, and the wider end is cut off so that only a short

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cut into a sheet of asbestos. The lower end of the tube which protrudes through the asbestos is heated with a naked flame until the contents boil. The thermometer reading at first rises, then remains constant for some time (this temperature is taken as the boiling point), and then rises again due to superheating. The best results are obtained by keeping the bulb of the thermometer at least 40 mm. above the level of the liquid, in order to avoid errors due to spattering of the superheated liquid. By this method triphenylamine gave 364.8° (corr.).

Yamagouchi (*J. Pharm. Soc. Japan*, **434**, 252 (1918); *Chem. Abs.*, **12**, 1528 (1918) has modified the simple apparatus of Pawlewski (*Ber.*, **14**, 88 (1881)) upon the principles of Siwoloboff's method.

Smith and Menzies, *J. Am. Chem. Soc.*, **32**, 897 (1910), describe a method not unlike that of Siwoloboff in principle. Their method has met with approval in the hands of several investigators, and the authors determined the boiling points of such a variety of substances as benzene, ether, camphor, naphthalene, calomel, etc. with a high degree of accuracy. For this method about 0.1 gram of the substance is used.—J. R. J.

[7] Schleiermacher, A., *Ber.*, **24**, 944 (1891).

piece remains. The tube is now bent to a U, so that the open arm is about twice as long as the closed one, the latter being about 15 cm. long. In order to do this, the tube is held in the flame at the proper place, allowed to fall about half way together, and is then bent around. The arms should be parallel and almost touch each other. The tube is now filled by dropping the sample into the open arm or by shaking a powder into it, and transferring it around the bend into the closed arm. Mercury is then run into the open arm (most conveniently from a burette with a stop cock, or from a paper funnel) until both arms are filled to about 2 cm. below the closed end. If the sample is liquid, it will have collected, of its own accord, over the mercury in the closed arm. If it is solid, and part has remained sticking to the wall of the closed arm, it is easily brought to the top by carefully heating until it melts. Any part of the sample which may have remained in the open arm does no damage. The material in the closed arm is now made to boil gently, and the air which has been absorbed by it, or on the walls of the tube, escapes through the fine capillary. Enough mercury is now

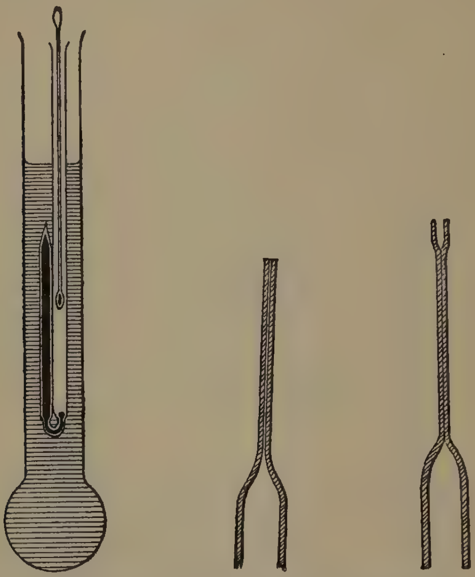

Fig. 162. Apparatus and Accessories (Schleiermacher)

added carefully so that the upper end of the open arm is filled up to the wide capillary with the liquid or liquefied material, and the fine capillary is then sealed off in the middle with a needle flame. If done properly, there remains in the point of the capillary only an extremely small bubble of air (or of a gaseous decomposition product) which has no influence on the accuracy of the determination, and is actually an advantage in that it prevents any delay in the boiling. Finally, the mercury is emptied from the open arm as far as the beginning of the bend, by turning the U-tube horizontally with the closed end down. The constriction at the bend prevents the escape of any liquid droplets from, and the entrance of a bubble of air into, the closed arm.

After the tube has been prepared in this way, it is placed in a heating bath. Water serves for materials boiling below 100°, while paraffin or sulfuric acid may be used for those boiling at a higher temperature. The heating tube of a Victor Meyer vapor density apparatus may be used as a container, if it is not too narrow. The U-tube is fastened in this, approximately vertical, and with its arms symmetrical to the axis, say by suspending it by means of a wire wound around it, so that the tube's lower end is about 10 cm. from the bottom of the container, and its capillary point about 5 cm. below the level of the liquid. The open end extends out of the heating liquid. The thermometer is hung in the open end at such a height that its bulb stands opposite the center of the vapor column in the closed end of the tube. The temperature of the vapor may be more accurately determined by placing the thermometer in the open tube, rather than immersing it in the heating liquid, because under these conditions, the vapor and the air, whose temperature is indicated by the thermometer, are under almost the same thermal conditions. Figure 162 shows the complete arrangement.

As soon as a bubble of vapor has formed, the heating is regulated so that the mercury in the closed arm sinks as slowly as possible; and at the instant the mercury menisci in both arms are at the same level, the thermometer indicates the boiling point at the prevailing height of the barometer. "The normal boiling point" under 760 mm. pressure can be just as easily determined even though the barometric pressure is not normal at that instant. If, for example, it is 750 mm., the mercury in the open arm is allowed to rise until it is 10 mm. higher than in the closed arm, and the pressure of the vapor is then exactly 760 mm., and its temperature is the normal boiling point. It suffices, for this purpose, to estimate the difference in height with the eye, or by means of rough calibrations (ink marks, slips of paper) placed on the heating vessel, since a difference of 3 mm. corresponds to a difference of only 0.1° (14 mm. = 0.5°) in the case of water. In determining the difference in pressure, no account need be taken of the drops of liquid, which at the most, are only several millimeters high. The boiling point is obtained more exactly if the levels of the mercury are moved first in one direction and then in the other, by alternately slightly increasing and decreasing the temperature of the heating liquid, and reading the thermometer each time the proper position is reached. In this way, there is obtained a series of figures which vary only slightly, and their average is taken as the desired boiling point.

The vapor tension method excels the distillation method with respect to the ease with which the normal boiling point may be determined, and offers still another advantage with reference to a source of error not always taken into account.

If part of the mercury thread of a thermometer extends beyond the space whose (higher) temperature is to be determined, the reading as is known, is too low. The extent of the correction to be applied cannot always be determined with certainty. When determining the boiling point by distillation, as a rule, (at higher temperatures) the larger part of the thread is outside the distillation flask, whereas in the method described, the thread is at almost the same temperature as that being determined, because the heating vessel is large enough to accommodate it. An example will possibly show that, at times, this correction is not inconsiderable. The aniline which was used in the observation cited below, when distilled from a flask, passed over at 179.5°. From the vapor tension the same thermometer showed the boiling point as 181.7°. The difference of 2.2° arises solely from the above correction, which may be calculated from the formula, $0.000156\ \alpha\ (t - t_0)$ discussed in the note on page 363.

Purity and stability of the substance and a correct thermometer are requirements common to both methods. The vapor tension method is, of course, limited to materials which are not decomposed by mercury, even at their boiling points. It is also limited to temperatures at which the tension of the mercury vapor itself is still inconsiderable. For very high temperatures, the mercury might be replaced by mobile alloys which, of course, are more difficult to handle. No influence of the vapor tension of mercury was observed up to 250°[8] or even at 300° and, therefore, it appears that the drop of liquid floating on the mercury seems to retard its vaporization for some time.

The smallest quantity of substance requisite for a determination is defined by the requirement that the vapor must be saturated, *i.e.*, that a trace of the liquid material must still be present as soon as the vapor fills the given space. If v is the volume in cubic centimeters of the vapor space; d the vapor density of the substance; and l the density of air at the boiling point (about 0.0012), then the required quantity is at least $v.\ d.\ l.$ With a tube of the dimensions given above, the vapor space has a volume of at least 2 cc. and consequently, 2 mgm. of water, for instance, would be necessary. Since an excess does no harm, it is better to always use more than this minimum quantity, as accidental impurities then have less influence.

It may be stated at the beginning, that in the following compilation of several observations with materials which were easy to obtain pure, that the mercury was only filtered through a paper funnel, but beyond this it was neither specially purified nor dried. The glass tubes were only cleaned by wiping them out with cotton. Temperatures up to 110° were taken with a corrected thermometer, higher ones with an uncorrected one. Therefore, these latter readings make no claims as to absolute accuracy, but the boiling points determined by distillation and by vapor tension are exactly comparable, since the same thermometer was used for both. The correction applied to the distillation point, because of the exposed mercury column, is placed in parentheses. With regard to the figures for the boiling points by the vapor tension method, those in the upper rows correspond to rising temperatures of the heating bath, those in the lower, to falling temperatures. Water and paraffin were used as the heating liquids, but brine was employed in the case of the water only, since in the paraffin bath the readings varied more because of the high heat of vaporization of water in contrast to the specific heat of paraffin. Comparison of the figures obtained by both methods is sufficient to show the reliability of the vapor tension method.

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[8] The boiling point of a small amount of diphenyl was found from its vapor pressure to be 251° which is in satisfactory agreement with the values between 250 and 251° given by various observers.

I. Carbon bisulfide, purified by repeated distillation over wax and mercury. Distillation point 46.8°.
From vapor tension: 46.7° 46.4° 46.8° Mean:
47.1° 47.1° 46.9° 46.8°

II. Water.
Vapor tension: 99.8° 100.1°
100.2° 100.0° Mean: 100.0°

III. Toluene "chemically pure." Distillation point given as 110.0°
Vapor tension: 110.3° 110.6° 110.2°
109.9 110.4° Mean: 110.3°

IV. Amyl alcohol, twice distilled. Distillation point: 130.1° (+0.7°)
Vapor tension: 130.3° 130.2° 129.9° 130.0°
130.2° — 130.3°
Mean: 130.2°

V. Aniline, twice distilled. Distillation point 181.7°. (+2.2°.)
Vapor tension: 181.7° 181.8° 181.6° Mean
181.5° 181.9° 181.6° 181.7°

VI. Naphthalene, twice distilled, Distillation point 214.6° (+3.6°)
Vapor tension: 215.0° 214.7° 214.6° Mean
215.5° 214.9° 214.9° 214.9°

Apparatus for this purpose has been devised by Main,[9] von Hasselt[10] and others.[11]

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[9] Main, P., *Chem. News*, **35**, 59 (1877).

[10] Hasselt, A., *Z. anal. Ch.*, **18**, 251 (1879).

[11] V. Arrequine has examined the methods of Siwoloboff and of Schleiermacher and has devised a modification of the latter, *Ann. chim. anal. chim. appl.*, **3**, 40 (1921); *Chem. Abs.*, **15**, 1845 (1921); see also Arrequine, (*Annales soc. quim. Argentina*, **3**, 133 (1915); *Chem. Abs.*, **10**, 3011 (1916).

Emich (*Monatsh.*, **38**, 219 (1917), *Mikrochemisches Praktikum*, p. 35, Verlag, J. F. Bergmann, Munich, 1924) describes a method which may be used with very small quantities of liquids. He asserts that observations may be made with 0.001 cc. of liquid.—J. R. J.

CHAPTER XVIII

SUBLIMATION

"Sublimation is frequently used in order to purify organic compounds. Usually, in such cases, there is none too much material, and the sources of loss are so numerous during the purification of organic materials by recrystallization, decolorization, etc. that because of the possibility of making a more exact study of such materials it appears of the greatest importance to reduce these losses to a minimum. However, the devices used for sublimation ordinarily do not fulfil this requirement at all, and chemists know their manifold disadvantages well enough." In 1855 Gorup-Besanez[1] made these statements concerning sublimations in the laboratory. Of the numerous methods which have been proposed since that time, that designed for working under reduced pressure seems best to the writer. Its most brilliant development has been sublimation in the vacuum of the cathode glow because, in it, even alkaloids, such as quinine and morphine, may be sublimed without decomposition, which may be of the greatest interest in the further study of these complicated natural products and their closely related degradation products.

Riiber[2] in 1900 states that there is hardly any method of preparing pure chemicals whose principle is so refined as sublimation. Without using a solvent, and therefore without loss, the desired material is obtained dry and crystalline, as well as free from unsublimable substances. It becomes of great value, especially when other methods are almost out of the question, as in the case of indigo, the higher hydroxyanthraquinones, etc., because of extremely slight solubility of the materials or because their boiling points are above the decomposition temperature. Unfortunately, in practice, it is only seldom that sublimation measures up to this ideal, since it is frequently accompanied by deep seated destruction of the material, and can then only be carried out with great losses. He also believes sublimation in a vacuum to be the best procedure, and has made his apparatus for this purpose (see below) as simple as possible.

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[1] Gorup-Besanez, E.-v., *Ann.*, **93**, 265 (1855).

[2] Riiber, C. N., *Ber.*, **33**, 1655 (1900).

SIMPLEST FORMS OF SUBLIMATION

The most simple arrangement for sublimation consists of two watch glasses laid upon each other with their edges together. Kolbe proposed that sublimation between watch glasses be carried out as follows: They are ground to fit each other; a piece of filter paper cut to the proper size, laid between them, and the whole arrangement held together by clamps made of two strips of brass. Gorup-Besanez made the further recommendation that they be heated on an air bath (fig. 163) whose temperature is indicated by a thermometer. The vapors of the subliming material are filtered, to a certain extent, through the paper septum and condense, usually in beautiful crystals on the inner wall of the upper watch glass which

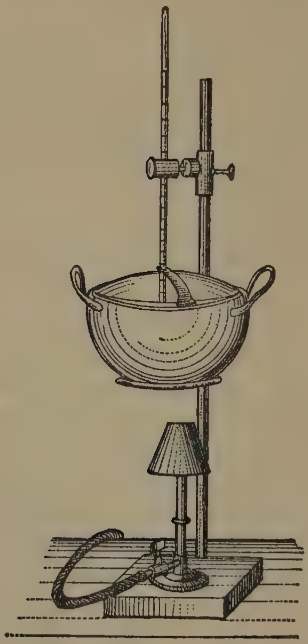

Fig. 163. Sublimation in Air Bath (Kolbe)

should have the greatest possible curvature. The upper watch glass is kept from becoming too hot by covering it with a small knitted cooling net, and ether[3] is cautiously dropped on it. The paper septum also prevents the sublimate falling back into the lower space which contains the non-sublimable residue.

According to Schützenberger, sublimation is accomplished by putting the dry material (1 gram at the most) in a wide porcelain crucible, 5 to 6 cm. high, and covering it with a round piece of filter paper and then with the lid. The crucible is heated in a sand bath. Fischer[4] also successfully used this procedure.

If other methods fail, the material may be spread evenly over the bottom of an Erlenmeyer flask which is loosely closed and immersed about 1 cm. in a sulfuric acid bath, provided with a thermometer. When no increase of the sublimate can be observed, the flask is removed from the bath, and if an analysis of the preparation is intended, the bottom of the flask is broken off, if necessary, to separate the sublimate from the residue.

Tollens[5] sublimed 1 gram portions of trioxymethylene in bomb tubes which were packed by means of asbestos in the iron tubes of the furnace so that the contents, (trioxymethylene) were within, but the empty portion of the tubes projected beyond the furnace, which was then heated to 180 to 185°.

The sublimability of salts of organic bases is exemplified by the hydrochloride of η-methyl α-pyridone, which Decker[6] found to sublime even on the water bath.

SUBLIMATION IN A CURRENT OF GAS

Larger quantities of materials are sublimed from a retort. Liebig[7] proposed that a current of an indifferent gas be introduced in order to remove the sublimate from the danger of further decomposition because of too high temperature, as well as to facilitate the sublimation in general. As a matter of fact, this did considerably increase the yield. Thus, with the aid of a current of carbon dioxide, he obtained over 80 per cent of the theoretical quantity of pyrogallol from gallic acid, when he heated a mixture of 1 part of gallic acid with 2 parts of coarsely pulverized pumice, in a retort. Up to that time, it had been obtained in much poorer yield by the method, devised much earlier by Braconnot,[8] of dry distilling gallic acid.

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[3] The use of ether is not permissible when the bath is heated by a flame. In such a case the glass should be cooled by a well-fitting soft filter paper or cloth continually moistened with water.—H. T. C.

[4] Fischer, Otto, and Hepp, Eduard, *Ber.*, **22**, 357 (1889).

[5] Tollens, B., *Ber.*, **15**, 1830 (1882).

[6] Decker, H., *J. pr. Ch.*, **29**, 155 (1893).

[7] Liebig, J., *Ann.*, **101**, 49 (1857).

Baeyer[9] recommends the following method for materials which are hard to vaporize. The bottom of a small, wide beaker is covered with the material. A low glass tripod supporting a sheet of paper which touches the walls, is then put in. A similar sheet of paper covered with a funnel is spread over the top of the beaker. A glass tube is passed through the neck of the funnel and the sheets of paper, almost to the bottom of the beaker. The beaker is then heated strongly and rapidly on a sand bath, while a vigorous current of carbon dioxide passes through the tube. At the end of the operation, the sublimate will be found between the first and second sheets of paper and on the inner wall of the funnel.

SUBLIMATION IN WATER COOLED APPARATUS

Sublimation apparatus provided with water cooling has been described by Brühl,[10] Landolt,[11] Hertkorn, and others.

Hertkorn[12] claims that his apparatus (fig. 164) is also very useful for subliming large quantities of iodine, such as are obtained by working up iodine residues. An enameled sheet iron funnel *B* has a wide opening in the cylindrical part which carries the cooling vessel *C*. The funnel is set into the channel *mm*, of the low pan *A* which is also made of enameled sheet iron. The cooling vessel *C* is fastened to the conical part of the funnel by a two-hole rubber stopper whose openings provide for the entrance (*a*) and outflow (*b*) of the cooling water. The exit tube *c*, which may be closed, is pushed through the second opening of the paraffined stopper. The seal between the funnel and the pan is made by pouring mercury, molten paraffin or plaster of paris into the channel, depending on the nature of the material to be sublimed. The channel serves to collect the liquid portions of the subliming material, and these drip away through the tube *d*. In this way, a partial distillation may be combined with sublimation which may be an advantage when dealing with wet materials or with mixtures. The material to be sublimed is covered with a porcelain plate *D*, with notched edges so that the sublimate will not fall back into the pan if the funnel should be jarred.

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[8] Braconnot, H., *Ann.*, **1**, 26 (1832).

[9] Baeyer, A., and Fraude, G., *Ann.*, **202**, 164 (1880).

[10] Brühl, J., *Ber.*, **22**, 238 (1889).

[11] Landolt, H., *Ber.*, **18**, 57 (1885).

[12] Hertkorn, J., *Ch. Zt.*, **16**, 795 (1892).

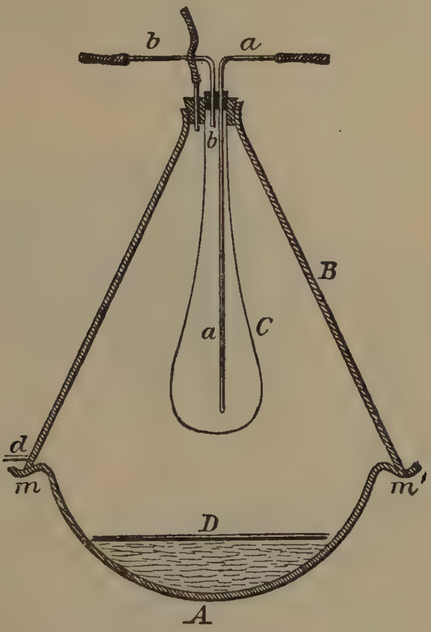

FIG. 164. SUBLIMATION APPARATUS (HERTKORN)

SUBLIMATION UNDER REDUCED PRESSURE

Kempf[13] has given an excellent and very extensive treatise on vacuum sublimation.

Sommaruga[14] was the first to attempt sublimation under reduced pressures. After trying in vain to purify indigo without decomposition by subliming it by one of the methods then known, he placed it in flasks of 70 to 80 cc. capacity, which were then evacuated to 30 to 40 mm. pressure. In this way, by heating the flask directly with a gas flame he could collect in the course of an hour any desired quantity of the sublimate.

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[13] Kempf, R., *J. pr. Ch.*, [2], **78**, 201 (1908).

[14] Sommaruga, E., *Ann.*, **195**, 305 (1879).

Bourgeois[15] also was able to sublime urea easily at reduced pressures, from a bath heated to 120 to 130°; under this treatment, thiourea was converted into ammonium sulfocyanate.

The writer believes that if quantities, which are not too large, are to be sublimed at reduced pressures, that it is best to place them in an open tube which is then put into a bomb tube. The latter is then evacuated as much as possible and sealed. The tube is then placed horizontally in a drying oven or metal bath, etc., so that the end in which the sublimate is to collect, projects into the open air. The tube is then heated.

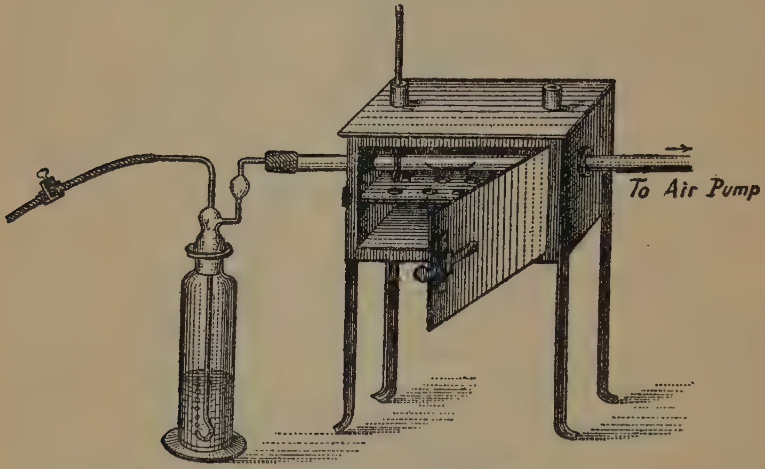

FIG. 165. SUBLIMATION UNDER REDUCED PRESSURE (LASSAR-COHN)

Vacuum sublimations in any desired gas may be carried out conveniently in the device which was first recommended by the writer for drying materials intended for ultimate analysis (see the heading "Analysis"). The crude material is placed in a platinum boat, which makes it convenient to remove the residual impurities later on, and this is then inserted into the glass tube passing through the drying oven (fig. 165). A current of any gas is drawn through the tube at a very low pressure which can be regulated by the screw clamp. The length of the glass tube may be so chosen so that the air cooling on the far side of the drying oven will suffice for the necessary condensation of the sublimate. Only in exceptional cases will it be necessary to wrap a moist cloth around it.

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[15] Bourgeois, L., *Bull.*, [3], **7**, 46 (1892).

The method of Riiber,[16] mentioned above, also only requires an ordinary water pump to produce the vacuum. The apparatus is heated in an iron double pan which is closed above with an asbestos plate, through which the sublimation apparatus and a thermometer are introduced. The apparatus (fig. 166) consists of a vertical glass cylinder *A*, which is connected above with an air pump through the tube *B*, and can be closed below by means of a ground glass cup *C*. The material to be sublimed is placed in *C*, an asbestos plate *D* laid loosely in the lower part of the cylinder *A*, which is then closed by the cup, and the whole device put into the air bath and evacuated. If the heat is gradually increased, at a certain definite temperature vapors will be evolved, which will condense to crystals in the colder cylinder *A*. His device of grinding the joint between the cylinder and cup so that it leaks a little, favors the sublimation considerably

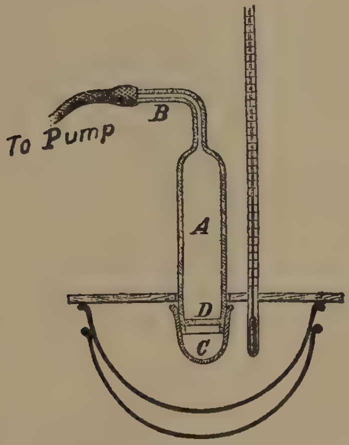

FIG. 166. (RIIBER) SUBLIMATION APPARATUS

since in this way, a little hot, rarefied air is constantly drawn over the material.

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[16] Riiber, C. N., *Ber.*, **33**, 1656 (1900).

Kempf,[17] whose work was mentioned above, uses for sublimation at reduced pressures, the simple apparatus shown in figure 167. The joints at *B* and *C* are ground. The form of *A* makes it possible to heat the material to be sublimed in any kind of a bath. The device is connected with the air pump by means of the tubing *E*.

SUBLIMATION IN THE VACUUM OF THE CATHODE GLOW

Krafft[18] used the same apparatus for the procedure which he developed for this purpose, as for his method of distillation under this vacuum discussed above (see fig. 71). While the thermometer bulb always remains bare during the distillation, it soon becomes covered with sublimate in this case, and this increases the difficulty of recognizing the sublimation temperature. But after a little practice even this point may be determined. In general, the determination of this temperature may be omitted, since it is usually of little importance. It is well to interpose an absorption vessel between the boiling apparatus, or the receiver, and the mercury air pump, because, if the material is not quite pure and dry, it is always difficult and often impossible to attain the high vacuum of the cathode glow.

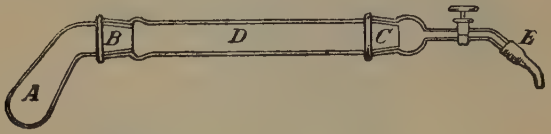

Fig. 167. Vacuum Sublimation Apparatus (Kempf)

Anthracene which boils at 351° at 760 mm. pressure, sublimes at 103 to 104°. Alizarine sublimes at 153°; chrysene boiling at 448° (760 mm.) at 169°. Camphoric acid of the correct melting point volatilizes at 163 to 164°, without loss of water or change in melting point. Caffeine sublimes rapidly and sharply at 116° (the temperature of the Wood's metal bath 170 to 200°); while the less volatile theobromine does not volatilize rapidly below 156°. Antipyrine may be conveniently distilled in the vacuum of the cathode glow because it boils under these conditions at 141 to 142°. Codeine which has a complicated structure, sublimes at 179°.

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[17] Kempf, R., *Ber.*, **39**, 3722 (1906).

[18] Krafft, F., and Weilandt, H., *Ber.*, **29**, 2240 (1896).

Rather slow sublimation, which often begins even at lower temperatures, is frequently of value in cases in which normal rapid volatilization causes decomposition of the pure or impure material. Thus commercial quinine sublimes very easily, even in a bath heated to 170 to 180°. However, if the Wood's metal is rapidly heated to a higher temperature, the quinine melts and begins to boil at about 210°, and this is soon followed by evidences of decomposition and rise of pressure. Morphine sublimed smoothly at 191 to 193° (temperature of the bath 275 to 280°), but the hard, solid crust of sublimate was somewhat yellow. Indigo sublimed in the vacuum of the cathode glow at 156 to 158°, but only when very pure.

The laboratories which produce pure preparations for the market will perhaps investigate the possibility of subliming their products under the vacuum of the cathode glow. It would be a great loss of time and effort to assemble the apparatus and to acquire the technique necessary for this type of sublimation for a single case, which might not be successful, even though it might prove to be the best method of purification. However, in case it proved practicable, it might perhaps save months of work or make it possible to continue studies which had come to an impasse.

CHAPTER XIX

DRYING OF SOLIDS AND DEHYDRATION OF LIQUIDS. DRYING OF GASES AND REMOVAL OF SINGLE GASES FROM GASEOUS MIXTURES

DRYING OF SOLIDS AT HIGHER TEMPERATURES

Solids are dried by heating them. If feasible, especially preparatory to analysis, they are placed in a tube preceded by a calcium chloride tube, and heated in an air bath in a current of dry air till constant weight is attained. The sublimation apparatus devised by the writer (fig. 165) is well adapted for this purpose also. The ordinary air baths consisting of single walled iron or copper chambers in which the temperature varies as much as 15° in different parts,[1] require a gas pressure regulator to maintain an approximately constant temperature in them. Considerable time is necessary and frequent attention must be paid to the apparatus before the desired temperature is established. If small quantities are to be dried, Victor Meyer's drying apparatus (fig. 168), which requires no supervision is preferable. It is made of copper, has double walls, and is arranged so that air may be passed through the working space. The constant temperature is insured by filling the space between the double walls with a liquid which boils at the desired temperature. The liquid is kept at the boiling point. The following liquids may be used for the temperatures given:

Chloroform	60°
Methyl-ethyl alcohol, 3:7	70°
Ethyl alcohol	75°
Ethyl-propyl alcohol, 7:4	80°
Ethyl-propyl alcohol, 1:8	90°
Water	97–100°
Toluene	107°
Xylene	136°
Anise oil	150°

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[1] Schuyten, M., *Ch. Zt.*, **30**, 369 (1906).

Cumene	161°
Aniline	180°
Naphthalene	200°
Diphenylamine	300°

The temperatures reached with these liquids in the air bath are somewhat lower than the true boiling points given in the table, because of the passage of the air current, which, however, greatly accelerates the drying. None of the liquids corrode metal, and consequently, the metal Soxhlet condenser is particularly suitable because it makes the apparatus unbreakable.

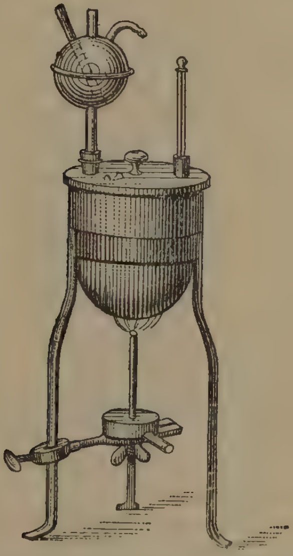

FIG. 168. DRYING APPARATUS (MEYER)

There are also on the market drying ovens made of strong cast metal, through the jacket of which steam may be passed at about 0.5 atmosphere superpressure, producing a temperature of about 110°.[2]

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[2] Christ. and Co., *Ch. Zt.*, 29, 990 (1905).

DESICCATORS

Materials are placed in desiccators if they must be dried at ordinary temperatures because they cannot withstand drying at higher temperatures. These vessels also provide a moisture-free space for storing materials which have been dried at higher temperatures. Since far more materials are decomposed by light than it is generally assumed, it is well to have available at least one desiccator made of dark glass.[3]

Among the dehydrating agents used in desiccators are concentrated sulfuric acid, phosphorus pentoxide, calcium chloride, lime, barium oxide, stick caustic potash, stick caustic soda and soda lime. If compounds lose carbon dioxide in the desiccator, they are dried in an atmosphere of this gas; if they lose ammonia, in an atmosphere of it, which may be produced by dropping a few slightly moist crystals of ammonium chloride on the solid caustic potash.

Müller-Erzbach[4] found that there is no essential difference between phosphoric anhydride, concentrated sulfuric acid and dehydrated potassium hydroxide in their attraction for water. Sodium hydroxide and calcium chloride containing little water, also differ only slightly in this respect. However, caustic soda can be completely dehydrated if confined with caustic potash, and there is only a difference of a fraction of a millimeter of mercury in the tension of the water vapor over phosphoric anhydride and over practically anhydrous calcium chloride. However, sulfuric acid[5] works much more rapidly than calcium chloride.[6]

According to Morley,[7] whose statements are indisputable, if the rate of flow of the gas and the drying tube are in the proper relation, sulfuric acid does not allow the passage of more than one milligram of moisture in 400 liters of gas, and phosphorus pentoxide is so superior as a drying agent, that the quantity of water vapor which was not absorbed amounted to perhaps only one per cent of this quantity.

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[3] Liebermann, C., *Ber.*, **21**, 2529 (1888).

[4] Müller-Erzbach, W., *Ber.*, **14**, 1096 (1881).

[5] The vapor pressure of sulfuric acid is not entirely negligible, and products, which are sensitive to acid vapors cannot safely be dried above it. Magnesium perchlorate is a valuable desiccating agent in such a case.—H. T. C.

[6] Fleischer, E., *Zeit. analyt. Chem.*, **23**, 33 (1884).

[7] Morley, E. W., *Z. ph. Ch.*, **20**, 91 (1896).

Hempel[8] called attention to the principal defect of the ordinary non-evacuated desiccators, which is that the drying agent is at the bottom of the vessel. Since moist air is lighter than dry air, there is only a slight exchange of the gas layers in the desiccator. In conformity with this fact, when he placed the drying agent above the material to be dried, he found that a quantity of water evaporated in three days which formerly required nine. However, the shape of his desiccators made them inconvenient. Reinhardt has devised the form shown in figure 169, which is just as easy to handle as those in common use. Their whole inner chamber may be used in the usual way. The turned up edge of the desiccator prevents the cover, ground to fit air tight, from falling off while the desiccator is being moved.

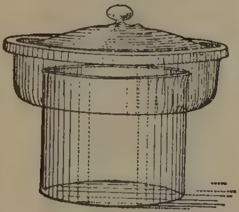

FIG. 169. DESICCATOR WITH ELEVATED SULFURIC ACID RECEPTACLE (REINHARDT)

If carbon bisulfide, ether, chloroform or benzene are to be evaporated in a desiccator, it is charged with pieces of low melting paraffin, instead of with sulfuric acid, etc. A solution of paraffin in paraffin oil that has solidified to a mush[9] is best. Liebermann[10] who was the first to make this observation states that the evaporation proceeds very rapidly. The paraffin liquefies, but without losing its absorption capacity. Carbon bisulfide is absorbed most rapidly, benzene most slowly. These solvents may be recovered in a very pure state by distilling the resulting paraffin solutions.

VACUUM DESICCATORS

All drying is accelerated by the use of desiccators provided with a tubulure by means of which they may be evacuated after charging.

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[8] Hempel, Walther, *Ber.*, **23**, 3566 (1890).

[9] Liebermann, C., and Finkenbeiner, H., *Ber.*, **28**, 2236 (1895).

[10] Liebermann, C., *Ber.*, **12**, 1294 (1879).

Evacuation of desiccators for hastening drying is due to Leslie.[11] A suitable grease for making them tight is given under the heading "Sealing of Corks, etc." Krafft states that loose barium oxide covered with asbestos paper is a particularly good drying agent for vacuum desiccators. By its use the water of crystallization of salts such as sodium acetate, zinc lactate, etc., may be determined.

Pflüger[12] states that good water pumps will evacuate a space to 11 mm. mercury pressure at a temperature of 16 to 20°. If boiled concentrated sulfuric acid is then admitted into the vacuum, the pressure rapidly falls to less than 1 mm. which indicates that a stream of water saturated with air removes all except minimal traces of the air from an enclosed space. Instead of boiling down small quantities

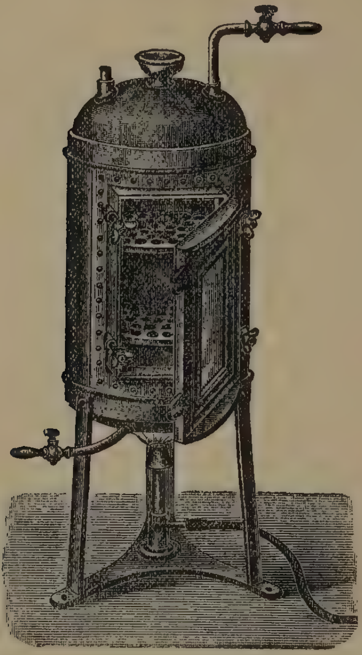

FIG. 170. VACUUM DRYING OVEN (HANFLAND)

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[11] Leslie: Faraday, M., *Chemical Manipulations*, 3rd ed., London, 1842, p. 263.

[12] Pflüger, E., *Pflüger's Arch. Physiol.*, **38**, 311 (1886).

of solutions, they may be allowed to evaporate in a desiccator, and this process is also accelerated by evacuation.

Vacuum drying ovens provided with heating devices may also be used in place of vacuum desiccators. The form shown in figure 170 is a double walled copper cylinder, and the working space may be surrounded with a boiling liquid. A reflux condenser may be fitted to the apparatus. The inner chamber is 22 cm. in diameter, 30 cm. high, and the door is 18 by 11 cm.

BEHAVIOR OF MATERIALS TO BE DRIED

Some substances offer special difficulties when being dried. Thus Schmiedeberg[13] found that the acid sulfates of chondroitin and chondroitin itself easily decomposed at 100° in a vacuum or under normal pressure. No constant weight was obtained by simply allowing these materials to stand over sulfuric acid, even for long periods. Usually merely drying over sulfuric acid in a vacuum at ordinary temperatures finally accomplished the desired result, but certain preparations required several months before they ceased losing weight.

Some series of materials, such as the tannins, retain organic solvents tenaciously. Therefore, it is advisable[14] before analyzing all materials of this kind which have been in contact with organic solvents, to redissolve them if possible, in a little water, and then dry them in vacuo.

Meyer and Hartmann[15] found that 1,3,6-trihydroxy-naphthalene intended for analysis, could not be dried in the usual manner, since the compound contained water which was given up very slowly at low temperatures, while the compound itself is volatile at higher temperatures. They finally accomplished their purpose by heating it to 100° in a current of dry air, while several calcium chloride tubes retained the water vapor given off. It is true that the compound constantly lost weight because of its volatility, but the weight of the calcium chloride tube which increased at first, finally became constant, and the drying was then considered complete.

If materials that cannot be dried by one of the usual methods, are to be extracted with ether, and so must have been dried previously, they may be treated in somewhat the manner in which brain substance is dried in the physiological laboratory. This is ground with a sufficient quantity of burned gypsum. After several days, all the water has combined as water of crystallization. The mass is ground again and may then be easily extracted.

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[13] Schmiedeberg, O., *Arch. Path. Pharm.*, **28**, 364 (1891).

[14] Fischer, E., and Freudenberg, K., *Ber.*, **45**, 920 (1912).

[15] Meyer, Richard, and Hartmann, Ernst, *Ber.*, **38**, 3951 (1905).

Finely ground flesh is also included in the class of materials difficult to dehydrate. Argutinsky[16] found that it loses water so slowly in a desiccator that the flesh begins to putrefy almost before the dehydration commences. Higher temperatures could not be used because they affect the flesh. After many experiments, he devised the following method, which he claims accomplishes a rapid and uniform drying without resorting to higher temperatures. The procedure may be applied to flesh (muscles) as well as to various other cellular materials, and to many other cases, and is said to accomplish the drying much more rapidly than the use of higher temperatures.

The process is essentially as follows: Four circular pieces, 15 to 16 cm. in diameter, are cut from a piece of nickel gauze and the edge of each piece is then bent upward with the fingers, to form a plate. Strips 2 cm. wide and 40 to 50 cm. long are cut from the same gauze and each strip bent to form a closed ring 10 to 12 cm. in diameter.

The pieces of gauze are carefully heated to clean them, and about 30 to 35 grams of the chopped flesh is spread out as thin as possible on each plate. After four pieces have been loaded in this way, they are piled on top of each other like plates, with one of the rings between each one as a support for the one above. The gauze stand, assembled in this way, is set on a piece of gauze covering a crystallizing dish containing a layer of pure sulfuric acid about 2 cm. deep. The dish and the stand together are then covered with a bell jar 18 to 20 cm. in diameter, and 30 to 35 cm. high, which is ground to fit a glass plate, and provided with a tubulure for evacuation. The flesh is completely dry after only twenty-four hours and can be kept indefinitely in the desiccator without decomposition. It is extremely hygroscopic if it is exposed to the air again.

DEHYDRATION OF LIQUIDS

Liquids are dried by adding to them: Aluminium amalgam; barium oxide; calcium; calcium bromide, chloride, iodide, carbide, nitrate, oxide, or sulfate; potassium bisulfate, ferrocyanide, hydroxide, or carbonate; copper sulfate; magnesium amalgam, magnesium sulfate; sodium; sodium hydroxide or sulfate; phosphorus pentoxide; sulfuric acid; silicon chloride; zinc chloride. The salts named above, which separate with water of crystallization are, of course, used in the dehydrated state.

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[16] Argutinsky, P., *Pflüger's Arch. Physiol.*, **55**, 347 (1894).

According to Brühl,[17] the water may be removed from liquids which boil at a high temperature, by passing carbon dioxide through the heated liquid.[18]

Calcium chloride loses 4 of its 6 molecules of water at 200°. When heated more strongly, the remaining 2 molecules of water are lost, and the anhydrous calcium chloride is left as a porous mass which in its turn, does not melt until 806° is reached.[19]

Potassium bisulfate melts at 197° with loss of its water.

Potassium ferrocyanide loses all of its water even at 100°.

Potassium carbonate still retains 5 per cent of the water at 100°, and stronger heating is necessary for complete dehydration. It melts at 878°.[20]

Copper sulfate does not lose all its water below 200°. The anhydrous compound is white.

Magnesium sulfate loses 6 molecules of water below 150°, the seventh only above 200°.

Sodium sulfate loses all its water of crystallization if exposed to the air, consequently, it may be dehydrated rapidly by heating. The anhydrous salt melts at 863°.[21]

Anhydrous zinc chloride forms an easily fusible mass.

QUANTITATIVE DETERMINATION OF SMALL AMOUNTS OF WATER IN LIQUIDS

Goetzl's[22] method may be used if it is necessary not only to remove the very small water content of a liquid, but also to determine quantitatively any residual moisture remaining after the drying.

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[17] Brühl, J. W., *Ber.*, **24**, 3391 (1891).

[18] Liquids such as benzene and toluene may readily be freed of moisture by distilling a small proportion and employing the residue.—H. T. C.

[19] Meyer, V., and Riddle, W., and Lamb, Th., *Ber.*, **27**, 3140 (1894).

[20] Meyer, V., and Riddle, W., and Lamb, Th., *Ber.*, **27**, 3140 (1894).

[21] Ibid.

[22] Goetzl, A., *Z. angew. Ch.*, **18**, 1530 (1905).

A rather large sample of the liquid to be tested is shaken with coarse grained, well dried calcium chloride free from dust, and after several days, an ultimate analysis of the original and of the dried liquid is made, and the difference represents the water content.

PARTICULARS CONCERNING DEHYDRATING AGENTS

Obviously only such drying agents are used for dehydrating liquids which have no chemical action on them. For example, chloroform is often dried with phosphorus pentoxide, pyridine with caustic potash. It might be stated as a general premise that it is preferable to dry the ether or acetic ester solutions, etc., so frequently obtained by shaking out aqueous solutions, only after the material dissolved in them has been separated as such. Thus Liebermann[23] dissolved hygrin in absolute ether and treated the solution with sticks of potassium hydroxide, in order to obtain the base entirely free of water, and also free of any carbon dioxide absorbed from the air. Sodium sulfate or magnesium sulfate are particularly suited for treating solutions of substances with which the drying agents may not react. Thus, Emil Fischer[24] pointed out that ether solutions of sensitive esters, such as those of the aliphatic amino acids must be dried with sodium sulfate, because the other drying agents, such as caustic potash, lime, barium oxide, and even potassium carbonate, decompose part of the ester after some time.

The water produced by a reaction may also be bound by a drying agent. For instance, sensitive oxidations, which must be carried out in absolutely anhydrous solution, may be accomplished by dissolving the material to be oxidized in anhydrous ether containing dry sodium sulfate to combine with the water produced by the oxidation, and silver oxide is then added.

CALCIUM CHLORIDE

Calcium chloride is most frequently used for drying, especially the fused form because it is not porous. However, it forms double compounds with many materials. For this reason, attempts are now frequently made to substitute other agents, such as sodium sulfate which shows this tendency only slightly under these conditions.

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[23] Liebermann, C., *Ber.*, **22**, 676 (1889).

[24] Fischer, Emil, *Z. physiol. Ch.*, **33**, 155 (1901).

Squibb[25] states that ether may be completely dehydrated by simply allowing it to stand for weeks with calcium chloride.

It cannot be used in the laboratory for drying alcohols—the preparation of absolute ethyl alcohol will be discussed presently—because it combines with them to form rather stable calcium chloride alcoholates which can only be completely decomposed by distillation from copper retorts. Liebig[26] was the first to point this out when he stated that methyl alcohol combines with calcium chloride to form a compound which does not decompose at 100°. In fact, Kane[27] later based a method of purifying methyl alcohol on the fact that the impurities of the alcohol separate as an oil when calcium chloride is added. As is well known, this purification is now accomplished by means of dimethyl oxalate which crystallizes well.

Propyl alcohol[28] combines with calcium chloride to form the compound $CaCl_2+3C_3H_8O$, which has the remarkable property of moving vigorously over the surface of the water until dissolved, although no gas is liberated. Warm benzyl alcohol dissolves so much calcium chloride that it solidifies into a crystalline mass on cooling.[29]

Lieben[30] states that fatty acids also combine with it to form crystalline compounds. It also forms compounds with many esters; for example, calcium chloride-ethyl acetate is known, and a calcium chloride-ethylgluconate of the formula, $C_6H_{11}O_7C_2H_5+CaCl_2$, likewise the corresponding compound of the ester of lactic acid.[31]

Calcium chloride also decomposes many compounds. Thus Thümmel[32] found that when oleic acid was dried with it, calcium oleate formed and the analytical results showed the oleic acid now contained chlorine. Roithner,[33] like his predecessors, used calcium chloride for drying ethylene oxide, until he discovered that moist ethylene oxide reacts with it to form lime and ethylene chlorhydrin.

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[25] Squibb, E. R., *Chem. News*, **51**, 66 and 76 (1885).

[26] Liebig, Justus, *Ann.*, **5**, 32 (1833).

[27] Kane, Robert, *Ann.*, **19**, 164 (1836).

[28] Göttig, Christian, *Ber.*, **23**, 181 (1890).

[29] Meyer, Richard, *Ber.*, **14**, 2395 (1881).

[30] Lieben, A., *Monatsh.*, **1**, 919 (1880).

[31] Schreiner, L., *Ann.*, **197**, 12 (1879).

[32] Thümmel, K., *Arch. Pharm.*, **228**, 285 (1890).

[33] Roithner, E., *Monatsh.*, **15**, 666 (1894).

From that time on, he dried the gas with soda lime. On the other hand, there is the remarkable observation of Ladenburg[34] that d-coniine d-tartrate may be dried at ordinary temperature over calcium chloride, but will not withstand drying over sulfuric acid.

Calcium chloride does not remove the last traces of moisture from all liquids. If this is of importance, as, for example, for exact boiling point determinations, sodium (for hydrocarbons), phosphorus pentoxide, or concentrated sulfuric acid should be used.

CALCIUM CARBIDE, CALCIUM IODIDE, AND CALCIUM NITRATE

Formerly, alcoholates were prepared by dissolving metallic potassium or sodium in alcohol. These alcoholates may now also be prepared by removing the water from alcoholic caustic potash, caustic soda, etc. This is based on the observations of Imbert and Krafft,[35] who found that calcium carbide possessed the requisite avidity for water. For instance, 60 kgm. of quicklime is added to a solution of 40 kgm. of sodium hydroxide in 300 liters of methyl alcohol, and after heating for some time, 8 kgm. of calcium carbide is added. After filtering, the resulting solution of sodium methylate is evaporated to dryness:

$$CH_3OH + NaOH - H_2O = CH_3ONa$$

Or, 56 kgm. calcium hydroxide is dissolved in 450 liters amyl alcohol and heated for some time after adding 40 kgm. calcium carbide. The filtrate consists of a solution of calcium amylate. It is claimed that these alcoholates may be used for all the condensation reactions for which the alkali alcoholates were formerly used. Polyatomic alcohols cannot be employed in this manner because decomposition sets in.

Calcium iodide may be used for drying hydriodic acid.[36] Calcium nitrate is hardly used except for drying sensitive nitro bodies, and also vapors of nitrous acid.

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[34] Ladenburg, A., *Ber.*, **27**, 3065 (1894).

[35] Imbert, G., and Krafft, W., German patent 164297 (1904); Fr. VIII, 23.

[36] Moissan, H., *C. r.*, **112**, 717 (1891).

ALUMINIUM AMALGAM, BARIUM OXIDE, CALCIUM, CALCIUM OXIDE, AND MAGNESIUM AMALGAM

Calcium oxide, aluminium amalgam (magnesium amalgam) and calcium are used chiefly for the preparation of absolute alcohol. Barium oxide has not found much favor for this purpose. Ordinarily, alcohol dehydrated by lime is satisfactory. Aluminium amalgam is useful for small quantities which are used quickly, and calcium is preferred if particularly dry alcohol is desired. As will be seen later, calcium is also the best means for preparing absolute methyl alcohol. If the absolute alcohol is to be free from aldehyde, the latter must be removed previous to the drying. A procedure for doing this has already been given in the discussion of the alcohols under the heading "Crystallization." There are various ways of preparing "absolute alcohol" with lime.

I. The alcohol is allowed to stand about two days[37] in the cold with much quick lime,[38] and is then distilled off. In this case, the lime is apparently little affected, but the alcohol which passes over (the first and last portions of the distillate being rejected) contains so little water that it is no longer colored red by potassium permanganate, but is scarcely brown. The rejection of the first runnings is easily understood; as was shown by Soubeiran,[39] the first portions of the distillate from nearly absolute alcohol, are richer in water. The last portions must be rejected because as Mendelejeff[40] has pointed out, the absolute alcohol at the increased temperature finally again withdraws water from the calcium hydroxide.

II. Commercial alcohol is boiled for one-half to one hour, on a water bath under a reflux with quick lime which must extend above the level of the alcohol. The condenser is then reversed and the alcohol which is now absolute, is distilled off. In this case, the lime falls to a powder as the hydrate is formed, and the heat suddenly set free usually causes the alcohol to boil up so that part of it is forced out of the condenser if the vessel is filled too full. If the alcohol contains more than 5 per cent water it must be subjected to this treatment two or more times.[41] If it contains very much water, the alcohol is boiled the first time with half its volume of lime, otherwise the rapid hydration will burst the glass container.

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[37] Mendelejeff, D., *Z. Chem.*, **1**, 260 (1865).

[38] Soubeiran, E., *Ann.*, **30**, 356 (1839).

[39] Soubeiran, E., *Ann.*, **30**, 360 (1839).

[40] Mendelejeff, D., *Z. Chem.*, **1**, 260 (1865).

[41] Erlenmeyer, E., *Ann.*, **160**, 249 (1871).

Barium oxide also is very well suited for preparing absolute alcohol.[42] Vincent and Delachanal[43] do not consider barium oxide suited for the dehydration of all alcohols. Allyl alcohol combines with it, forming the compound $2C_3H_6O \cdot BaO$. Hübner and Lellmann diluted this alcohol with 3 to 4 volumes of chloroform and then dried with calcium chloride (?). Even Raimundus Lullus attempted to dehydrate alcohol with potassium carbonate, but it is too weak a dehydrating agent to be used with alcohols. Thus Tornöe[44] showed that aqueous allyl alcohol which had stood in contact with ignited potassium carbonate until the latter removed no more water from it, still contained considerable water. According to a patent,[45] absolute alcohol may also be obtained by treatment with sodium sulfide.

The alcohol has lost the last portions of water as soon as the supernatant liquid turns yellow. The barium oxide must be prepared by decomposing the nitrate with gradually increased heat, since barium hydroxide loses none of its water even under strong ignition, and barium carbonate also is extremely stable toward heat.

If a little barium oxide is added to the alcohol after it has stood for some time with lime, the appearance of the yellow color, after standing sometime longer in the cold, indicates that the alcohol has been completely dehydrated. Sodium and sodium amalgam are not suitable for this dehydration because, according to Mendelejeff,[46] the distillates contain sodium and mercury.

So much lime must be added to dehydrate the alcohol that the residue, after distilling off the absolute alcohol, is very difficult to remove from the flasks, in fact, most of them break when this is attempted. The writer avoids this by supplementing the study made by Squibb,[47] who found that alcohol could not be as completely dehydrated by any of the laboratory methods then known, as it was on a large scale, in which it was slowly filtered in the cold

[42] Berthelot, M., and St. Gilles, Pean de, *Jahres bericht*, **15**, 392 (1862).

[43] Vincent, C., and Delachanal, B., *C. r.*, **90**, 1360 (1880).

[44] Tornöe, Hercules, *Ber.*, **24**, 2671 (1891).

[45] Chemische Fabrik, Griesheim Elektron, Frankfurt a M. German patent 236591 (1909); *Ch. Zt. Repertorium*, **35**, 435 (1911).

[46] Mendelejeff, D., *Z. Chem.*, **1**, 260 (1865).

[47] Squibb, E. R., *Z. anal. Ch.*, **26**, 94 (1887); *Ch. News*, **51**, 7 (1885).

through quick lime. According to him, alcohol prepared in this way, has a lower specific gravity than could be attained by any other method. Hence the writer proceeds as follows: A cylindrical tin plate vessel (fig. 171), higher than it is wide, having a capacity of 20 liters, is closed above by a well fitting cover and has a cock at the bottom. It contains a perforated sieve-like insert almost as high as the cylinder. A tube nearly as high as the apparatus is fastened in the middle of the bottom of the insert. The insert is filled with quick lime and as much alcohol as possible poured over it. After eight to fourteen days it may be drawn off through the lower cock as absolute alcohol. The same lime may be used three to four times if the depression caused by its contraction is refilled each time. The fine lime sludge which clogs the cock is pushed down by a wire inserted through the middle tube whenever absolute alcohol is to be drawn from the apparatus. The whole apparatus is hung on the wall. It is best to keep it constantly filled with lime and alcohol; the used lime may be removed by lifting out the insert which has a handle for this purpose. The apparatus has given good service for many years without requiring any repairs.

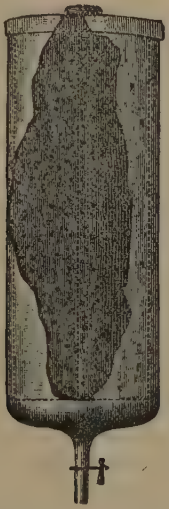

FIG. 171. APPARATUS FOR THE PREPARATION OF ABSOLUTE ALCOHOL (LASSAR-COHN)

Alcohol dissolves extraordinarily little lime. Smith[48] states that 50 cc. of alcohol syphoned from the lime deposit and then filtered, left less than 0.0005 gram of residue. Filtering alcohol prepared by the above method, purifies it sufficiently for many purposes, such as the maceration of preparations for medical purposes for instance. If it is distilled, it is found to be over 99.9 per cent.

Wislicenus and Kaufmann[49] have found aluminium amalgam to be another agent for completely drying alcohol. They found that this amalgam is a reducing agent with very remarkable properties, and at the same time, they also discovered its suitability for the present purpose. It requires only a few minutes to prepare the amalgam, their method being as follows: Aluminium turnings freed of oil are treated with sodium hydroxide solution until there is a strong evolution of hydrogen. They are then washed superficially with water. The corroded metal, which is still slightly wet with sodium hydroxide, is then allowed to react for one to two minutes with an approximately 0.5 per cent solution of mercuric chloride. This whole operation is quickly repeated in order to remove the black deposit which forms, and the amalgam is rapidly and thoroughly rinsed with water, alcohol and ether in turn. If necessary, the preparation may be stored under low boiling petroleum ether. The last traces of water adhere very firmly and after a short time may cause so vigorous a reaction that the petroleum ether begins to boil. Aluminium "activated" in this way, reacts with water just as do the alkali metals, but has absolutely no action on alcohol. It will react however, with the slightest trace of water contained in alcohol. Considerable hydrogen is evolved when it is placed in so-called absolute alcohol.[50] Consequently, amalgamated aluminium is just as excellent a means of completely drying alcohol, as sodium is for ether.

Young has taken out an English patent on a procedure for obtaining anhydrous alcohol, without the use of a drying agent.[51] It is based on the observation that a mixture of water, alcohol and benzene distils in constant proportion, and boils at a lower temperature than any of its three components. Furthermore, a mixture of alcohol and benzene also distils in constant proportion and boils at a lower temperature than either of these two materials alone, but at a higher temperature than a mixture of the three. Therefore, if a mixture of them, for instance, 90 to 94 per cent alcohol and benzene, is distilled, a mixture of all three passes over first at the lowest temperature until the distillate contains all of the water. If the distillation is continued, a mixture of alcohol and benzene distils until all of the benzene also has passed over. Comparatively pure alcohol remains in the distilling vessel and is now distilled in turn. The distillation, carried out in a column apparatus, is continued until the boiling point of pure alcohol is reached, the alcohol being collected separately. The impure alcoholic distillates are put back into the next run.

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[48] Smith, J. L., *Chem. News*, **30**, 235 (1874).

[49] Wislicenus, Hans, and Kaufmann, Ludwig, *Ber.*, **28**, 1325 (1895).

[50] Amalgamated aluminum also reacts with absolute alcohol to form aluminum ethoxide.—H. T. C.

[51] Young, S., *Ch. Zt.*, **27**, 687 (1903).

According to Konek[52] really absolute alcohol is prepared most conveniently by boiling commercial absolute or even 96 per cent alcohol with an excess of 2 to 10 per cent magnesium amalgam. After one to two hours, the alcohol is distilled from the mercury and magnesium hydroxide. Absolute alcohol so prepared shows the same physical constants as that obtained by means of metallic calcium.

The best method of preparing anhydrous alcohol was published by Winkler[53] in 1905. He uses turnings of commercial calcium. Since these are usually contaminated with considerable quantities of calcium nitride, the latter must be removed as much as possible, so that the alcohol obtained does not contain ammonia. The turnings are well sifted through a rather coarse mesh gauze and most of the calcium nitride falls through. The traces of petroleum adhering to the metal are removed by vigorously shaking the turnings with dry carbon tetrachloride (or any other suitable solvent) in a glass stoppered bottle, collecting them in a loosely closed funnel and then rinsing with carbon tetrachloride. This also serves to remove as much as possible any nitride still adhering to the turnings. These are dried in the air or in a current of carbon dioxide until the odor has vanished. About 20 grams of the metal, which now contains only small quantities of the nitride, is added to each liter of the commercial alcohol to be dried, or of absolute alcohol dried in the laboratory with lime. In order to remove the ammonia from the anhydrous distillate, several centigrams of alizarin are dissolved in each liter,

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[52] Konek, F. v., *Ber.*, **39**, 2263 (1906).
[53] Winkler, L., *Ber.*, **38**, 3612 (1905).

10 cc. of the alcohol taken out and about 0.5 gram dried tartaric acid dissolved in this. This latter solution is then dropped into the colored alcohol until it becomes a pure yellow. Several drops more of the tartaric acid solution are added and the alcohol is again distilled, the air being excluded as much as possible.

According to Gyr,[54] calcium is also particularly suited for removing the last vestiges of water from methyl alcohol. Pure methyl alcohol which however, still contains water, reacts very sluggishly in the cold, but the reaction speeds up if it is warmed slightly. The distillation is postponed until most of the calcium has become a dirty gray mass. The first portions of the distillate have an unpleasant smell. The later distillate may be treated three or four times more with calcium this being necessary for complete drying. The reaction with the calcium becomes more vigorous with each treatment, and finally is almost explosive. The hydrated oxide which forms on the surface of the metallic calcium is brittle and breaks off easily, constantly exposing fresh surfaces of the metal.[55]

SODIUM AND SODIUM-POTASSIUM ALLOY

Sodium is used for drying hydrocarbons, but chiefly for preparing anhydrous ether. However, potassium-sodium alloy is preferable for this purpose.

Ordinarily, the ether is pre-dried with calcium chloride or phosphorus pentoxide. As mentioned above, calcium chloride alone is said to be capable of completely dehydrating ether if they are allowed to stand together for some weeks. However, Timpe[56] has found that sulfuric acid of proper strength is also very suitable for this. According to him, crude ether becomes absolute, even without distillation, if it is shaken with sulfuric acid of the proper concentration. In his experiments, the yield of absolute ether, density 0.7220 at 15°, was 59 to 60 per cent of the crude ether, when 38 per cent sulfuric acid was used. This constitutes a convenient and rapid method by which the small quantities of dry ether so often needed, may be prepared hurriedly in a test tube. The residue which has gone into the acid, consists chiefly of alcohol and ether. These are distilled off and reused, while the acid may be used many times for purifying the ether, because 31 per cent sulfuric acid is still capable of completely drying ether, but the drying is incomplete if 27 per cent acid is used.

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[54] Gyr, Joseph, *Ber.*, **41**, 4323 (1908).

[55] Austerweil, G., This is also of interest with other liquids dried over calcium, *e.g.*, terpentine, see German patent 211799 (1909), Fr. IX, 1139.

[56] Timpe, H., German patent 124230 (1901); Fr. VI, 24.

The long established use of sodium for drying ether will now be discussed. Only the surface is active, even though the metal is cut into very thin pieces, because it becomes covered with a white, smeary layer which prevents the underlying portions from reacting.[57] Consequently, it is much better to use the liquid potassium-sodium alloy. This has been mentioned in connection with the more recent thermometers designed for high temperatures. The writer[58] studied this question considerably in connection with another piece of work and formulated the following method for drying ether.

If about 2 parts of potassium and 1 part of sodium are pressed together under warm petroleum in a porcelain dish, the liquid alloy is formed. Sodium and potassium[59] easily form alloys which are still liquid at 0° if they contain from 0.33 up to 10 parts of potassium, to 1 part of sodium. If they contain too much sodium they are brittle and crystalline. The alloy obtained by heating 10 parts of sodium and 16 parts potassium under petroleum, is similar to mercury and becomes mushy at 8°. The potassium is preferentially oxidized in all of these alloys. If the alloy is poured into pre-dried ether, which is then boiled under a reflux condenser, it floats on the surface as a metallic sphere, in contrast to metallic sodium which sinks. It remains perfectly bright since the potassium or sodium compounds formed settle on the walls of the flask. Consequently, very little of this alloy is required for complete drying, since it is entirely consumed in the ether, in contrast to the large quantity of sliced sodium needed.

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[57] Attention should be called to the fact that the addition of water to considerable quantities of sodium is almost certain to lead to violent explosions. An assistant in the writer's laboratory was seriously injured when he allowed water to run into a flask containing slices of sodium covered with a smeary coating. These had been used for dying large quantities of ether, more sodium being added from time to time. Sodium residues may be destroyed without danger by throwing it on a coal fire in a stove having a good draught.

[58] Lassar-Cohn, *Ann.*, **284**, 229 (1895).

[59] Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg, 1906, vol. II, p. 461; see also Mellor, J. W., *Inorganic and Theoretical Chemistry*, vol. II, p. 480, London (1922).

Nef[60] assumed that ether dried with sodium is never perfectly anhydrous, because if fresh pieces of sodium are added after it has been distilled, some gas is always evolved. Perhaps ether distilled over phosphorus pentoxide with all precautions will not do this, though nothing is known about it. Consequently, if it is necessary to know whether sodium really reacts on a dissolved compound, dry benzene or petroleum ether, rather than ether, should be chosen as solvent. If these are used, even the minutest liberation of gas can be ascribed with certainty to the dissolved material and not to the solvent.

Any water content, exceeding the last traces, may be detected in ether which is supposed to be dry, by the turbidity which appears when the ether is mixed with an equal volume of carbon bisulfide. The presence of alcohol is betrayed by the color which appears when shaken with aniline violet. Alcohol-free ether develops no color.

SILICON CHLORIDE AND ZINC CHLORIDE

On one occasion, Ladenburg[61] freed ethyl acetate of the last traces of alcohol and water by means of silicon chloride, and Friedel and Crafts[62] ascertained that aqueous alcohol is made absolute by heating it to 100° with the ester of silicic acid. Hartmann[63] used zinc chloride to dry petroleum.

DRYING OF GASES AND REMOVAL OF SINGLE GASES FROM GASEOUS MIXTURES

The drying of gases is effected by the inorganic hygroscopic materials which have already been mentioned as suitable for drying liquids. Particular attention must be paid as to their indifference toward the gas, as instanced by the behavior of ethylene oxide toward calcium chloride discussed above.

The practicability of using "active charcoals" for absorbing gases from gaseous mixtures was discussed under the heading "Decolorization."

With the exception of water vapor, *i.e.*, moisture, approximately the following other gases can be removed from gaseous mixtures by methods which are generally applicable. While acid gases are absorbed by alkalies, and alkaline ones by acids, chlorine may be removed from a mixture of gases by passing the mixture over heated antimony. Bromine is removed by red phosphorus. According to Than,[64] carbon bisulfide vapor may be removed by passing the mixture through a tube filled with caoutchouc, and hydrogen cyanide by passing it over cotton mixed with moist mercuric oxide. The mixture is passed over solid chromic acid[65] to abstract sulfur dioxide, and Hauser[66] separates carbon monoxide and hydrogen from methane by adding oxygen to the mixture and then passing it over palladium and rhodium asbestos at a temperature not exceeding 180°. The methane remains unchanged while the carbon dioxide and water may easily be removed later.[67]

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[60] Nef, J. U., *Ann.*, **287**, 332 (1895).

[61] Ladenburg, A., *Ber.*, **3**, 305 (1870).

[62] Friedel, C., and Crafts, J., *Ann. ch. ph.* [4], **9**, 36 (1866).

[63] Hartmann, E., *Ber.*, **24**, 1019 (1891).

[64] Than, C., *Ann.*, Suppl., **5**, 236 (1867).

[65] Szasz, E., *Ch. Zt.*, **39**, 483 (1915).

[66] Hauser, E., *Ch. Zt.*, **32**, 783 (1908).

[67] This whole subject is treated exhaustively by Moser, L., in his "Reindarstellung der Gasen," Sluttgart, 1920.

CHAPTER XX

DETECTION AND DETERMINATION OF NITROGEN, THE HALOGENS AND OF SULFUR IN ORGANIC COMPOUNDS; THE ASHING OF ORGANIC MATERIALS

WITH REFERENCE TO ULTIMATE ANALYSIS

This field has developed extensively during the past few years because many new methods have been introduced, but so far none of these has entirely displaced the older procedures.

A. Weighing of the sample to within 0.1 milligram

Arndt[1] remarks with respect to the time consumed in weighing by many chemists, who attempt to determine the fractional parts of a milligram by moving the rider back and forth between the milligram marks of the balance beam, that it is simpler to place the rider on the next milligram mark and estimate the tenths by observing the swings. This requires a knowledge of the center of oscillation and also of the sensitivity of the balance, *i.e.*, how many more divisions of the scale the pointer will pass over when an excess load of 1 mgm. is on the other side. For instance, if the sensitivity is five scale divisions, a swing of three additional scale divisions toward the right, means that 0.6 mgm. must be added to the weights on the right. It is sufficient to observe two swings of the pointer to one side and one to the other. In ordinary chemical weighings, it is unnecessary to know the exact center of oscillation; in weighings which closely follow each other, and in which only the difference is taken into account, it may be assumed to be the same as the center point of the scale, because in the difference between the weights, for instance, of a platinum crucible weighed empty and then with contents, any error made because of this assumption does not enter. The tedious complete equalization of the loads on both arms of the balance is no more exact than the method of swings just described, which is used exclusively in physical laboratories, because the center of oscillation, also known as the zero point, usually changes slightly each time the balance is arrested. Furthermore, the balance is saved by not arresting it so often, and careful treatment of a balance is of prime importance, or should be, to anyone who desires to make exact weighings.

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[1] Arndt, K., *Z. angew. Ch.*, **16**, 1253 (1903).

B. Drying the sample

The writer dries every solid intended for analysis, to constant weight. Unless this precaution is taken, the agreement of the analytical figures depends more or less on chance. The material to be analyzed is placed in a glass tube which passes through the walls of a drying oven, in which it can be heated to the proper temperature (fig. 172). The tube is connected with an air pump and the air drawn through the tube must pass through a layer of sulfuric acid. A considerable vacuum can be obtained by properly adjusting the screw clamp, so that even very sensitive materials may be treated in this way. The pump rapidly removes every trace of moisture from the evacuated space. Two successive weighings at an interval of fifteen minutes will indicate when the drying has been completed.

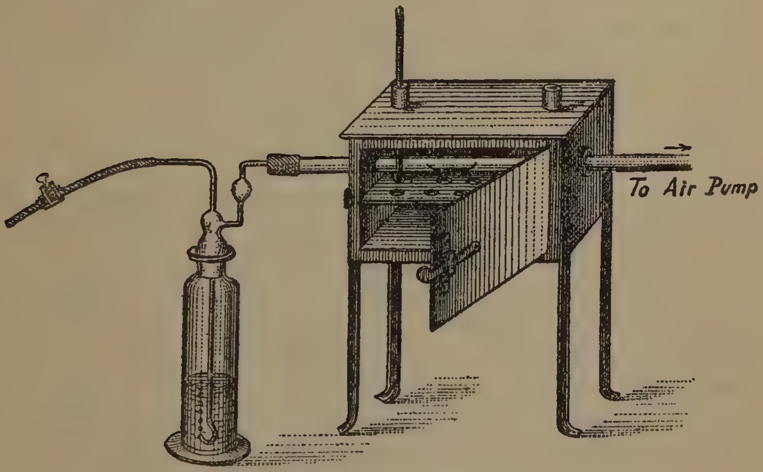

FIG. 172. DRYING OF ANALYTICAL SAMPLES (LASSAR-COHN)

If a material loses hydrochloric acid or ammonia when dried in this way, the gas is absorbed in a standard solution or determined gravimetrically.

DETERMINATION OF NITROGEN

A. Qualitative

(*a*) *By means of soda lime*

Nitrogen is most simply detected in organic compounds, not ammonium salts of acids, nitrates of bases, nor diazo compounds, by following Wöhler's suggestion of heating with soda lime in a small tube, and observing whether ammonia vapors are evolved. This less sensitive method is not nearly as good as the following one originated by Lassaigne.[2]

(*b*) *By means of potassium or sodium*

Lassaigne's method is to heat the material to be tested, with a little potassium (sodium is usually used now) in a small glass tube until it glows. After cooling somewhat, the tube is allowed to slide into a test tube containing several cubic centimeters of water, held at an angle and turned away from the operator. (Caution!) The small tube breaks, and to the clear liquid obtained by filtration is added a solution of ferrous sulfate in ferric chloride, followed by hydrochloric acid. If a blue coloration or a blue precipitate appears, nitrogen is present. The origin of the blue precipitate is, of course, due to the sodium combining with the nitrogen in the presence of carbon, to form sodium cyanide which reacts with the iron salts in the warm alkaline solution to form sodium ferrocyanide. When the solution is acidified, the excess ferric salt present reacts with the ferrocyanide and forms Prussian blue. Jacobsen[3] has called attention to the fact that this old established method sometimes fails, namely, when the organic material contains sulfur in addition to the nitrogen.

In this case, from amino-sulfonic acids, thiourea, etc., for example, a thiocyanate of the alkali metal is formed in place of the cyanogen compound. Only in exceptional cases do such materials, when heated alone, produce carbon so rich in nitrogen and poor in sulfur that the test succeeds with them. The following modification due to Jacobsen is claimed to overcome this difficulty. It is based on a partial conversion of the potassium sulfocyanate into potassium cyanide by iron. A small granule of the sample is mixed with at least four to five times its volume of iron powder, and this mixture is melted with potassium or sodium, exactly as in the Lassaigne method. The cold melt is covered with water and the solution filtered after a few minutes. A few drops in excess of hydrochloric acid are added to the filtrate, which is then treated with a dilute solution of ferric chloride containing ferrous sulfate. Of course, a mixture of the iron powder and an organic compound free from nitrogen, such as sugar, should give no blue, or at the most, only a greenish cast, when subjected to this test.

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[2] Lassaigne, J. L., *Ann.*, **48**, 367 (1843); *C. r.*, **16**, 387 (1843).

[3] Jacosben, Oscar, *Ber.*, **12**, 2317 (1879).

In spite of this, Täuber[4] claims that the Jacobsen method may lead to false results, because finely divided iron is itself a nitrogen carrier, and so may cause the air to take part in the formation of cyanide. According to him, this source of error may be eliminated only if hydrogen is passed over the reaction mixture.

According to Graebe,[5] it is still possible to detect nitrogen in materials containing nitrogen and sulfur, in spite of the presence of the sulfur if, contrary to the present usage, the Lassaigne method is again adopted, but very much more potassium is used. The excess plays the same part as the iron in the Jacobsen modification of this method. However, the nitrogen of diazo compounds can practically never be detected in this way, because it escapes before the action on the alkali metal takes place. Täuber[6] has found the Graebe method to be excellent, except for diazo compounds. He uses about 0.02 gram of the material and 0.2 gram freshly cut potassium, and heats them carefully at first, until the metal melts, and then heats about two minutes, up to incandescence. The melt is then quenched in 6 to 8 cc. water.

Kehrer[7] states that the Graebe-Täuber procedure fails with certain pyrrole derivatives. However, these cases may be successfully

[4] Täuber, Ernst, *Ber.*, **32**, 3150 (1899).

[5] Graebe, C., *Ber.*, **17**, 1178 (1884).

[6] Täuber, Ernst, *Ber.*, **32**, 3154 (1899).

[7] Kehrer, E. A., *Ber.*, **35**, 2523 (1902).

handled, if a glass tube not too wide, is drawn out sharply on one side and the material to be tested put into the narrowed portion. The alkali metal must not be placed too near the sample. After the metal has been heated to glowing, the test portion is heated very slowly by means of a second flame, and the vapors pass over the glowing metal. Even the most varied pyrrole derivatives reveal the presence of nitrogen when treated thus. The test is finished in the usual way.

(c) *By means of a mixture of potassium carbonate and magnesium powder*

Castellana[8] states that the nitrogen in any organic substance can be infallibly detected if the nitrogenous material is heated with a mixture of potassium carbonate and magnesium powder. This mixture liberates potassium in the nascent state,[9] and this is certainly the basis of its very special usefulness for the purpose at hand. The writer believes that this procedure will supersede that of Lassaigne and all its modifications, because the mixture of potash and powdered magnesium can be kept in readiness, and consequently, the inconvenience of working with small bits of potassium or sodium which must be specially cleaned each time, is eliminated.

Winkler recommends a mixture of 138 parts of potassium carbonate and 72 parts of magnesium for this liberation of potassium:

$$K_2CO_3 + 3\,Mg = 2\,K + C + 3\,MgO$$

According to Castellana, several milligrams of this mixture are mixed on a piece of platinum foil with the material to be tested, and then heated in a porcelain crucible or in a glass tube sealed at one end. The residue is then tested for potassium cyanide. More detailed directions are not given in his paper. The writer uses the following procedure:

The solid or liquid to be tested for nitrogen is mixed with a little of the mixture made with ignited potash, and is then put into the lower part of a glass tube which has been drawn out and sealed off. The fluffy mixture easily fills the lower half of the narrow part of the tube, and more of the mixture free of the organic material is placed over it. The upper part of the tube is heated first in the flame; glowing ensues and carbon separates. The heating is now continued until finally the glow has extended through the part containing the organic material. After cooling, the part of the tube which was in the flame is broken into a porcelain dish containing a little water, and crushed with a porcelain pestle. The filtrate, because it is only slightly alkaline is treated with a few drops of sodium carbonate solution, and a ferric chloride solution containing some ferrous sulfate is then added. It is heated slightly and then acidified with hydrochloric acid and any blue coloration or blue precipitate indicates the presence of nitrogen in the original sample.

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[8] Castellana, V., *Gaz. chim.*, **34**, 2, 359 (1904).

[9] Winkler, Clemens, *Ber.*, **23**, 45 (1890).

B. Quantitative

Nitrogen is determined quantitatively by the methods of Dumas, Kjeldahl, or Will-Varrentrapp. Pregl's micro-determination of nitrogen has recently been added to these, but reference only will be made to this since he has described it at length in his excellent book, "Quantitative Organic Micro-Analysis."[10]

According to Gehrenbeck, it is possible to determine the hydrogen content of the sample along with the nitrogen by the Dumas method. Fritsch has found that a wet carbon determination can be combined with the Kjeldahl method. In this way, these methods which are suited to nitrogenous materials, permit the simultaneous determination of two constituents and so in many cases, a complete ultimate analysis can be dispensed with. This economy is accomplished frequently enough by being satisfied with the determination of nitrogen alone, but it is impossible to judge how many false conclusions have arisen from this very convenience. Quite a few such cases are known.

The comparison of the Dumas, Kjeldahl and Will-Varrentrapp methods carried out long ago by L. L'Hôtes,[11] showed a difference in the results, only if the sulfuric acid in the second procedure was still colored even after heating for one and one-half days, which could hardly occur now with a properly chosen oxidizing agent. The difference was probably due to a slight volatilization of ammonium sulfate during the prolonged digestion.

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[10] Fischer, Hans, *Ber.*, **51**, 1323 (1918); Pregl, Fritz, *Quantitative Organic Microanalysis*, translated by Fyleman, New York (1926).

[11] L'Hôte, L., *C. r.*, **108**, 817 (1889).

(*a*) *Dumas' method*

A hard glass tube much narrower than those used for ultimate analyses (C+H) is employed in Dumas' method. One end is sealed, and a material which evolves carbon dioxide when heated, is placed in this end of the tube. An asbestos plug follows. Some copper oxide is shaken on this and then follows the sample to be analyzed, well mixed with powdered cupric oxide. The tube is then filled with more copper oxide, but space is left for a roll of bright copper. Finally, a channel, large enough to permit the passage of the gases is formed by tapping the tube, since otherwise, the gases will push the contents of the tube ahead of them, and spoil the analysis. After the tube has been filled with carbon dioxide by heating, and the sample burned, carbon dioxide, water vapor and nitrogen will be obtained. The nitrogen is collected over potassium hydroxide and measured. (O'Sullivan[12] claims that 4 to 11 per cent of nitric oxide is always mixed with this nitrogen).

It should also be noted, that although copper oxide usually suffices as the oxidizing agent, nevertheless, there are times when it may become necessary to use lead chromate, which is far more efficient. Thus, Möhlau and Fritsche[13] found that when copper oxide was used in the analysis of octomethyl-tetra-amino-phenylacridine, $C_{27}H_{33}N_5$, 1 per cent too little nitrogen was always obtained, whereas with lead chromate, 16.68 per cent instead of 16.39 per cent nitrogen was found. (Kjeldahl gave 16.17 per cent).

The writer uses coarsely broken magnesite as the material for liberating carbon dioxide in the tube. It is thoroughly dried in an oven before being used. He also permits the evolution of carbon dioxide to proceed at first with the tube open, which is thus rapidly filled with the gas. If the carbon dioxide is not liberated until after the apparatus designed to receive the nitrogen has been connected with the tube, the impact of the bubbles passing through the liquid ahead causes the carbon dioxide to be continuously mixed with the air still left in the tube, and obviously it will require much longer to completely expel it.

According to Ilinski,[14] manganese carbonate is also very good for this generation of carbon dioxide. It is only slightly hygroscopic, furnishes a very uniform current of gas, and the progressive decomposition may be recognized by the gradual browning of the material.

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[12] O'Sullivan, James, *Ber.*, **25**, R, 804 (1892); *J. S. C. I.*, **11**, 327 (1892).

[13] Möhlau, Richard, and Fritsche, E., *Ber.*, **26**, 1042 (1893).

[14] Ilinski, M., *Ber.*, **17**, 1349 (1884).

If nitrogenous materials are so sensitive that they are decomposed even by slightly warmed carbon dioxide, or are volatilized to a considerable extent, the carbon dioxide cannot be generated from magnesite, etc., but must be drawn from a carbon dioxide generator. A rapid current of the gas is passed, though not for too long, through the combustion tube whose rear end has been drawn out to a capillary. For instance, Fischer[15] carefully mixed the phenylhydrazine salt of phenylcarbazinic acid with powdered copper oxide in a fine glass tube, which was then completely filled with copper oxide and placed in a tube charged as usual. After the air had been displaced by a rapid current of cold carbon dioxide (whose preparation free from air will be found later in the discussion of the simultaneous determination of nitrogen and hydrogen) the capillary at the rear end of the tube was sealed off, while the forward gas delivery tube was dipped into mercury. The material in the narrow tube was then transferred to the combustion tube by careful tapping, and the combustion carried out as usual.

Materials hard to burn are mixed with a little mercuric oxide in addition to the copper oxide, but not much should be used, so that the oxygen liberated later will certainly be completely absorbed by the forward copper spiral.

Many materials may require very special treatment. For instance, Duden determined the nitrogen content of dinitromethane although it decomposes in a few minutes even at room temperature, and consequently, an ultimate analysis is entirely unpracticable. He cooled it very strongly, weighed it rapidly and immediately diluted it with a little ether. This solution was then introduced into the combustion tube, and 25.63 instead of 26.98 per cent of nitrogen was finally obtained.

The cupric oxide used for these analyses should be treated just like that employed in carbon-hydrogen determinations, but in this case, its hygroscopic properties need not be considered.

On the other hand, the copper spirals required for decomposing the oxides of nitrogen are much more conveniently prepared than those used for C+H analyses. They are prepared by strongly heating the rolls in the blast lamp, and immediately dropping them into a test tube containing a few drops of warm methyl alcohol. This evaporates very rapidly and the vapor instantly reduces the spiral which is protected from reoxidation by inserting a well fitting cork as soon as the reduction is complete.

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[15] Fischer, E., *Ann.*, **190**, 124 (1878).

It has been shown more than once that copper rolls do not reduce all oxygen-nitrogen compounds sufficiently for this analysis. Thus Deninger[16] found the nitrogen contained nitric oxide, in spite of the spiral, when he analyzed *o*-hydroxydiphenylamine and its derivatives. He made the copper more active by mixing the front layer of copper oxide with sugar, and thus produced in the tube much more finely divided copper, and this actually did completely prevent the appearance of nitric oxide.

Bader and Stohmann,[17] as mentioned above, encountered difficulties in the combustion of substituted naphthylamine sulfonic acids and overcame them with the aid of cupric oxide-asbestos. The volumetric determination of nitrogen also failed when applied to most of this class of compounds, until they developed the following modification of the procedure.

The combustion tube *A-B* (55 cm. long), of the proper width, (fig. 173) is charged with a rather loosely packed layer of cupric oxide-asbestos (*b*) 20 cm. long, which is held in place on each side by a plug of pure asbestos. Behind the copper oxide-asbestos layer is placed a reduced copper gauze spiral (*c*) 10 cm. long, which should fill the tube as much as possible. The tube is enveloped at *b* and *c* with brass gauze as a protection against too strong heating, and a 10 cm. shield of this gauze (*e*) which also may be easily pushed over the tube, is placed over the rear portion of the tube intended for the boat. The copper spiral is removed, and the tube is burned out from the rear to the front, in the direction of the arrow, in a current of oxygen, during which the movable brass-gauze shield (*e*) (see the description of the preparation of the copper oxide-asbestos) is gradually moved toward *b*, and is slowly followed by the burner. After the tube has cooled, the reduced copper spiral is put in place, the boat introduced and carbon dioxide passed through the tube. The boat which should be about 1 cm. from the rear asbestos plug (α) contains the finely pulverized sample intimately mixed with the finest copper oxide powder, and then carefully covered with the latter material. As soon as all of the air has been expelled, the flames at *b* and *c* are lighted, and also the burner which heats the gauze shield *e* to redness, and the shield and burner are gradually moved toward the boat, taking care that the carbon dioxide current through the tube is not too slow, since otherwise the sample or its combustion products may easily sublime toward *B*. This may also be prevented by keeping *B* warm by placing a clay tile, like a roof, over the tube. The analytical figures obtained are very satisfactory.

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[16] Deninger, A., *J. pr. Ch.*, [2], **50**, 90 (1894).

[17] Bader, R., and Stohmann, A., *Ch. Zt.*, **27**, 663 (1903).

Considerable difficulty was found by Pauly and Rossbach[18] to attend the determination of nitrogen by the Dumas method (using cupric oxide of course) in the methyl and also the ethyl ester of tetramethyl-pyrroline-carboxylic acid, because unburned carbon monoxide was liberated very easily during the combustion. In the case of the ethyl ester it was found impossible to completely burn the carbon monoxide formed, even though the greatest care was taken. Consequently, they found it necessary to allow the gas obtained to stand over cuprous chloride solution until there was no further diminution in volume.

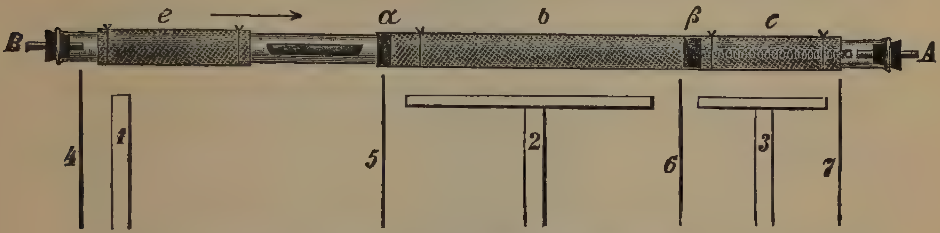

FIG. 173. MODIFIED PROCEDURE FOR THE DETERMINATION OF NITROGEN (BADER AND STOHMANN)

It has already been mentioned that Haas found as much as 6 per cent too much nitrogen when he determined this element in diresorcin-phenylene diamine, the excess being due to methane mixed with the nitrogen collected. Since, as was stated above, the hydrochloride of such bases can be burned successfully, he mixed the free base with cupric oxide and with three to four times its weight of cuprous chloride, and then determined the nitrogen with the aid of lead chromate.[19] The results were very satisfactory, 8.02 per cent instead of 7.95 per cent nitrogen being found. Possibly the bases could have been burned directly in the presence of lead chromate with equally good results.

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[18] Pauly, Hermann, and Rossbach, Joseph, *Ber.*, **32**, 2013 (1899).

The solution of potassium hydroxide over which the nitrogen is to be collected, must be very strong because it should absorb the carbon dioxide almost instantly. This is very essential, since otherwise, the lye will be forced out of the azotometer by the unabsorbed gas. The solution is prepared by dissolving 1 part solid caustic potash in 2 parts of water. A solution of caustic soda cannot be used at all for this purpose.

Numerous proposals have been made with reference to the apparatus for collecting the nitrogen. Ilinski[20] has compiled the material published on this subject up to 1883. The writer also was particularly interested in this subject and for more than 25 years used only the following azotometer.[21] In the meantime, a number of other chemists have used it without further modification, with the exception of the new method of constructing the cock *H*, to be presently discussed.

The gas generated in the combustion tube enters the tube *B* of the azotometer through the small tube *A*, which can easily be moved by means of the rubber connection. The shape of *B* is shown in figure 174. It is made of bent barometer tubing so that it is rather durable though somewhat narrow. The form itself makes it difficult for the caustic potash to suck back into the combustion tube. This is made almost impossible by blowing at *C*, where the barometer tube continues as the wider tube *D*, a small bulb in which a little mercury is placed to separate the solution of potassium hydroxide from the combustion tube delivering the carbon dioxide. The considerable pressure exerted by even a small amount of mercury is readily made evident by blowing into this or similar apparatus. In order to protect the combustion tube, which tends to soften when heated to redness, not more mercury than is absolutely necessary should be used to separate the potash lye from the current of carbon dioxide.

The tube *D* which serves for measuring the nitrogen is divided into tenths of cubic centimeters, and has a cock *H* at the top. Above this cock, the tube is again widened to its original bore for a short length, and is then narrowed so that the rubber tube *G* may be fastened to the end. The other arm of the tube *D* has a funnel shaped end *F*. A glass tube over which a rubber tube with a screw clamp is slipped, is sealed into the bottom of this arm of *D*.

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[19] Haas, P., *J. Ch. Soc.*, **89**, 574 (1906).

[20] Ilinski, M., *Ber.*, **17**, 1347 (1884).

[21] Lassar-Cohn, *Festschrift für Jaffe*, Braunschweig, 1901.

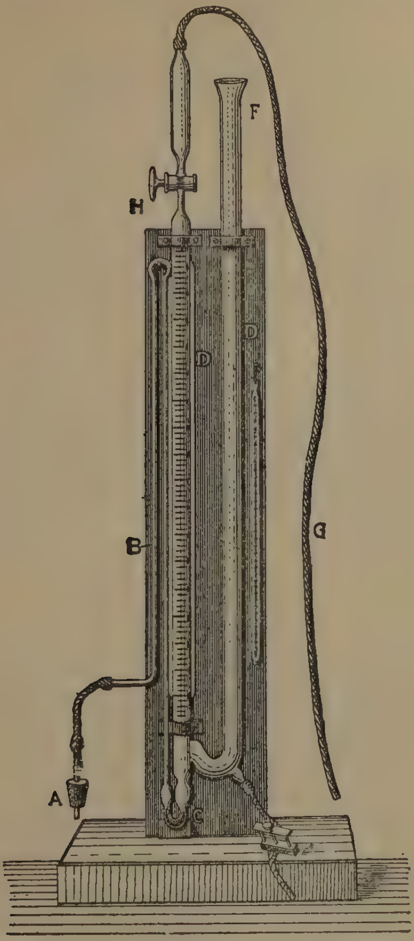

FIG. 174. AZOTOMETER (LASSAR-COHN)
The stopcock *H* is of glass with a metal valve for alkaline liquids

The caustic potash lye is poured into *F* until both arms of *D* are about three-fourths filled, the cock *H* being open. The mercury at *C* prevents the solution from rising too high in *B*, since it is pushed upward by the lye, and because of the narrowness of the tube it rises and remains about half way up in it.

It is also advisable when displacing the air, to allow the carbon dioxide to be generated for some time with the tube open. If after a short time, most of the air has been removed from the combustion tube, the azotometer is connected with it, and the caustic solution is sucked up above the cock *H*, by means of the tube *G*. The widened portion of the tube above *H* prevents the lye being sucked into the mouth of the operator. Any air bubbles which pass over later, collect below the cock and are removed, from time to time, by opening it and sucking on *G*. When, finally, pure carbon dioxide is coming over, the nitrogen determination is carried out in the usual way.

When the determination is finished, the collecting device is disconnected from the combustion tube and lye poured into the open arm of *D* until the level is about the same as in the closed arm. After the nitrogen has reached room temperature, the level of the caustic potash is made the same in both arms, so that the gas is under the prevailing barometric pressure, and the volume of nitrogen is then read. The thermometer fastened to the stand indicates the room temperature.

After the reading is finished, the caustic solution is drained off through the lower tubing which can be closed by the screw clamp. The tubing is of black rubber and lasts for years. The small quantity of caustic solution, which as may be seen, finally is left over the mercury in the barometer tube and below the drain, and so cannot be emptied out, may be left indefinitely in the apparatus, since it does not affect subsequent determinations at all.

The construction of the cock *H* will now be discussed. It is well known that ordinary cocks used continuously for alkaline liquids, fail after a time because the water glass forming on the ground surfaces gradually seals the cocks so they cannot be opened. Of course the cock *H* of the writer's azotometer had the same fault. This led him to consider whether it would not be possible to replace the ordinary glass cock by one which would not be attacked by alkaline liquids, but which could still be sealed into glass apparatus. Early attempts were unsuccessful, but finally the problem was solved in the following simple manner (fig. 175). The key of the ordinary glass cocks was replaced by a metal cock of the same form, and ground to fit very exactly. Attempts to use hard rubber or metal keys failed. In this way, the glass unit remained unchanged externally and could thus be sealed into apparatus of any design as before, while the alkaline liquid, after the metal cock is put in place, flows between two metal surfaces which it does not affect; consequently, it can never make this cock stick. Such cocks made of phosphor bronze, nickel or silver have been on the market since 1905 and have been found perfectly tight when tested with an air pump. They have been rather widely adopted, especially for burettes. A method of connecting glass with metal was published in 1921.[22]

Graebe[23] discusses azotometers in which the levels of the caustic

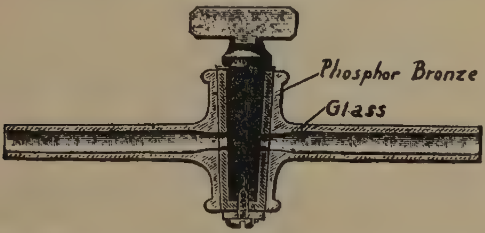

FIG. 175. GLASS STOPCOCK WITH METAL VALVE FOR ALKALINE LIQUIDS (LASSAR-COHN)

solution inside the tube containing the nitrogen and outside cannot be equalized, and points out that if the volume of the nitrogen is read while it is confined over 30 to 33 per cent caustic potash, the millimeters do not correspond to the barometer reading reduced to 0°. The tables ordinarily used for calculating which give the weight of 1 cc. of nitrogen at different temperatures and pressures, may be used directly for nitrogen measured over caustic potash, without marked error, provided the barometer reading taken at the same temperature is not reduced to 0°. Strictly speaking, when using such tables, the barometer reading should be reduced to 0°, and to it should then be added the difference between the tension of water vapor and that of the caustic potash solution. However, these two values almost compensate each other so that the difference between the figure to be subtracted and that to be added, amounts to less than one millimeter and may therefore be disregarded.

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[22] *Deutsche Glasinstrumentenzeitung*, p. 34 (1921).

[23] Graebe, C., *Ann.*, **276**, 9 (1893).

If a table is not available from which the weight of the volume of nitrogen found in the analysis may be directly read, the weight may be calculated by the formula:

$$W = \frac{V\,(h - w)}{760\,(1 + 0.00367\,t)} \times 0.0012562.$$

In this, V signifies the observed volume in cubic centimeters; h the barometer reading, and w the tension of water vapor or of the potassium hydroxide solution at the temperature t. Errera's table for the tension of the caustic solution is shown in table 11. The weight of 1 cc. of nitrogen at 0° and 760 mm. pressure is 0.0012562 gm.

TABLE 11

Tension of potassium hydroxide solution

TEMPERATURE	$\frac{40\text{ KOH}}{100\text{ H}_2\text{O}}$	$\frac{49\text{ KOH}}{100\text{ H}_2\text{O}}$	TEMPERATURE	$\frac{40\text{ KOH}}{100\text{ H}_2\text{O}}$	$\frac{49\text{ KOH}}{100\text{ H}_2\text{O}}$
	mm.	*mm.*		*mm.*	*mm.*
10.00	6.50	5.62	17.00	10.26	8.88
11.00	6.95	6.01	18.00	10.93	9.47
12.10	7.47	6.46	19.00	11.65	10.09
13.00	7.93	6.86	20.00	12.40	10.75
13.95	8.44	7.30	21.00	13.20	11.44
15.15	9.11	7.88	21.82	13.88	12.04
16.00	9.62	8.33			

(α) Simultaneous determination of nitrogen and hydrogen

According to Gehrenbeck,[24] this analysis is carried out in a combustion tube open at both ends and charged in the usual way. Particular attention must be paid to thoroughly mixing the sample with finely powdered cupric oxide or lead chromate. The rear end of the tube is closed with a stopper through which a two way cock passes. One arm is connected with the apparatus such as is used also in ultimate analysis for drying oxygen and air, the other arm with the drying apparatus of the carbon dioxide generator. This may be any apparatus which delivers air-free carbon dioxide, such as a glass tube charged with sodium bicarbonate, lying free in an iron tube. The weighed calcium chloride tube is connected with the other end of the combustion tube and to this the apparatus for collecting the nitrogen. A calcium chloride tube which need not be weighed is placed between these so that no moisture from the azotometer may reach the weighed calcium chloride tube.

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[24] Gehrenbeck, Clemens, *Ber.*, **22**, 1695 (1889).

The analysis is made by filling the apparatus with carbon dioxide, which requires about three-fourths to one hour, and then the determination of nitrogen is carried out as usual. When the volume of nitrogen ceases to increase, the azotometer is taken off, the two way cock turned and first oxygen and then air is passed through the apparatus as in a C + H combustion, and the calcium chloride tube is then reweighed. The analysis takes about two to two and one-half hours and check analyses give satisfactory results. The method has been highly recommended by Kehrmann and Messinger[25] also. They generated the carbon dioxide in a Kipp apparatus, and behind the sulfuric acid drying vessel they placed another tube containing fused and coarsely broken potassium carbonate, so that hydrochloric acid vapors, which would have increased the weight of the calcium chloride tube, could not enter the combustion tube. The air was removed as much as possible from the hydrochloric acid used in the Kipp apparatus by boiling, and from the marble by evacuation. Long ago Hufschmidt[26] had shown that the error due to air is reduced to a minimum by this means. In his analyses, he allowed boiling hydrochloric acid to react with marble in a suitable apparatus, after it had been found that 3 liters carbon dioxide generated in this way contained only 0.2 cc. of gas not absorbed by potash lye. Three years previously, Bernthsen[27] had recommended that marble be freed of air by covering it with water in a thick walled flask which is then evacuated, and occasionally shaken. He states that the results leave nothing to be desired.

(*b*) *Kjeldahl's method* (*also for nitro bodies*)

Kjeldahl[28] originated the wet method for quantitatively determining nitrogen. Its principle is to heat the sample for some time with

[25] Kehrmann, F., and Messinger, J., *Ber.*, **24**, 2172 (1891).

[26] Hufschmidt, F., *Ber.*, **18**, 1441 (1885).

[27] Bernthsen, A., *Z. anal. Ch.*, **21**, 63 (1882).

[28] Kjeldahl, J., *Z. anal. Ch.*, **22**, 366 (1883).

a considerable quantity of concentrated sulfuric acid, to a temperature somewhat near the boiling point of the acid, in the presence of agents which accelerate the oxidation. The ammonia produced is distilled off and determined by titration.

Since the reagents used, sulfuric acid, caustic soda solution, etc., are not entirely free of nitrogenous compounds, their nitrogen content is determined once for all and subtracted from the results obtained. For this reason a quantity of the reagents sufficient for a large number of analyses is prepared at one time and a Kjeldahl is run with these on a nitrogen-free material such as sugar, which gives the nitrogen content that must be taken into account.

Mitscherlich[29] has perfected Kjeldahl's method for determining nitrogen to the highest degree. He succeeded in making nitrogen determinations whose limits of error were only ±0.000012 gram. He did this by eliminating, as much as possible, all the sources of error attending the usual procedure, such as that arising from the alkali content of the glass, etc. In general, the results by the following methods will be satisfactory.

There is as yet no general agreement concerning the agent to be added to the concentrated sulfuric acid; potassium permanganate originally used has been displaced by copper sulfate and mercury,[30] etc. Later, Gunning[31] proposed potassium sulfate and it, as well as mercuric oxide, (see below for details) have been found convenient and effective.[32] Gunning uses a mixture obtained by melting 1 part potassium sulfate with 2 parts of ordinary sulfuric acid. The mass is semi-solid at room temperature, but it melts easily and can be conveniently poured out of heated vessels. The sample, 500 to 1000 mgm., is placed in a round bottom flask of about 300 cc. capacity (much larger quantities of organic materials, 100 grams of flesh, for example, can easily be decomposed in larger flasks) with a short neck, and heated over a Bunsen burner with 20 to 30 cc. of the mixture. Liquids are first brought to incipient dryness in the flask with the addition of some acid, if necessary.

Strong foaming occurs at first, and acid, along with much water, is evolved, and later stronger acid escapes. However, according to

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[29] Mitscherlich, E., *Z. angew. Ch.*, **22**, 631 (1909).

[30] Argutinski, P. Compare *Pflüger's Arch. Physiol.*, **46**, 581 (1891).

[31] Gunning, J., *Z. anal. Ch.*, **28**, 188 (1889).

[32] Dyer, B., *J. Ch. Soc.*, **67**, 811 (1895).

Arnold and Wedemeyer,[33] this strong foaming does not take place if a mixture of 3 parts sulfuric acid and 1 part potassium sulfate is used. This loss of acid and the consequent concentration of the acid in the flask may, of course, not be carried too far. This can easily be controlled because the acid vapors can almost all be condensed and made to flow back if a well fitting funnel whose opening is closed with a watch glass, is set in the mouth of the flask.

As soon as the foaming subsides, the apparatus may be left to itself and if the flame is so regulated that the evaporating acid flows back regularly down the walls, carrying with it the adhering carbonaceous materials, the reaction is accomplished in a short time. If no metal oxides which impart a color are present, a white product is obtained which, after cooling, may be dissolved, and the procedure continued. The time required for the decomposition is not always the same; frequently one-half hour suffices, occasionally less, but the digestion with the acid mixture never takes more than one and one-half to two hours. Duplicate analyses check very well.

Krüger[34] has written extensively on the use of potassium dichromate as oxidizing agent in this method of determining nitrogen. A further development of this method led Fritsch to the simultaneous determination of carbon and nitrogen (see below).

There is little to be said concerning the apparatus if a well drawing hood for the removal of the sulfur dioxide generated is available. If this is not the case, Vogtherr's apparatus (to be described later) may be used. With its aid, the decomposition of the organic material, as well as the subsequent distillation of the ammonia, may be accomplished in the same apparatus with no inconvenience from sulfurous acid.

Dafert,[35] who has extensively investigated the applicability of the Kjeldahl method, has concluded that nitrogenous materials may be divided into two classes, namely: (1) Those which can be analyzed by this method without pre-treatment; and (2) those which require preliminary treatment.

Among the materials which may be treated directly by the Kjedahl process he includes: all amines and ammonium bases, the pyridine and quinoline bodies, the alkaloids, the bitter materials, the albumins and related substances. In all probability, the derivatives of indole also belong in this class. To the second group belong, with certain exceptions, all nitro- nitroso- azo- diazo- hydrazo- and aminoazo bodies; the compounds of nitric and of nitrous acids; the hydrazines and probably also the cyanogen compounds. Thus Thiele[36] states that aminoguanidine derivatives yield only a part of their nitrogen by the Kjeldahl process, and in particular, amino-tetrazotic acid,

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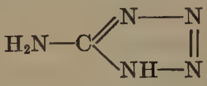
[33] Arnold, C., and Wedemeyer, K., *Zeit. f. analyt. Chem.*, **31**, 526 (1892).

[34] Krüger, Martin, *Ber.*, **27**, 609 (1894).

[35] Dafert, F., *Z. anal. Ch.*, **27**, 224 (1888).



gives only about one-fifth. According to Delépine,[37] the Kjeldahl method is not suited for the chlorplatinates either. He obtained results far too low when he analyzed the chlorplatinate of ammonia and of trimethylamine. He believes the reason is that chlorine is liberated from the platinic chloride and sets free the nitrogen of the base:

$$(NH_4)_2\,PtCl_6 + 3\,Cl_2 = PtCl_4 + 8\,HCl + N_2$$

Dafert found the following preliminary treatment to be the best for nitro bodies: The sample is dissolved in 10 cc. alcohol (or if it is very resistant, directly in ordinary concentrated sulfuric acid), zinc dust is added and it is then warmed, with the addition of 10 cc. of concentrated sulfuric acid, until the alcohol has been completely volatilized. When this has been accomplished, there is added a little mercury and 10 cc. of the acid mixture recommended by Kreusler (1 liter concentrated sulfuric acid and 200 grams phosphoric anhydride). The subsequent procedure is the same as usual. The nitroso bodies and also an azoxy compound tried by Dafert, yielded very good results when treated in this or a similar manner.

Chenel[38] states that nitro compounds should be reduced with iodine and phosphorus in order to determine the nitrogen in them by the Kjeldahl method. For instance, he treated nitronaphthalene thus and the naphthylamine obtained by the reduction yielded very close results.

As Werhahn[39] has stated, the nitrogen of even gun cotton may be

[36] Thiele, J., *Ann.*, **270**, 56 (1892).

[37] Delépine, M., *C. r.*, **120**, 152 (1895).

[38] Chenel, L., *Bull. soc. chim.*, [3], **7**, 324 (1892).

[39] Werhahn, B., *Ch. Zt.*, **16**, 1278 (1892).

determined with great accuracy by the Kjeldahl method. About 0.5 gram nitrocellulose is placed in a small flask, and 15 cc. of pure concentrated sulfuric acid, containing 6 per cent of phenol, is poured over it. This last mixture was recommended by Jodlbauer.[40] The flask is repeatedly swirled until solution is complete. Then 5 grams pure crystallized sodium thiosulfate is added, and the flask again swirled, until the reaction which ensues has ceased, in order to keep the strongly foaming mixture from bubbling over. Then 0.5 gram of mercury and 15 cc. more of pure concentrated sulfuric acid are added and the flask is heated until the digestion is complete.

It may be assumed from this that the nitrogen of all nitro compounds may be determined by the Kjeldahl method provided they are subjected to proper preliminary treatment.

The decomposition of organic fertilizers, vegetable materials and soils, for the purpose of determining the nitrogen by the Kjeldahl method, is occasionally unpleasantly disturbed because the boiling sulfuric acid mixture begins to bump violently after most of the reaction is over. Many materials are so unruly that the Kjeldahl flask is thrown off the digestion rack. There is not much improvement if the flasks are tightly clamped by the neck, because then there is danger that the bottom of the flask will be broken out. Since the bumping of the boiling liquid is due mainly to the presence of grains of sand, this may be remedied according to Mastbaum, by transferring the liquid to another flask in which the digestion is then completed. Better results are obtained if a flask is used which has a small excrescence projecting sharply from the wall of the lower third of the flask (fig. 176). As soon as the bumping begins, the sand grains are allowed to collect in the excrescence and the flask is turned slightly on its axis so that the liquid is obtained as clear as possible. The boiling is then continued until the digestion is finished. This device is very effective.

The writer uses the following procedure with mercuric oxide[41] as catalyst. The sample, which may contain up to 0.03 gram nitrogen, is placed in a long necked flask holding about 150 cc. Weighed samples of solids are allowed to glide into the flask in a boat,[42] and in this way the sample is prevented from adhering to the neck of the flask. The sample may also be wrapped in a filter paper.[43] The liquid samples are run in directly from a pipette. 7 to 8 cc. of sulfuric acid containing 15 per cent SO_3, is then added. This should not be sucked up in a pipette because of the danger to the experimenter, but should be measured from a small graduated cylinder. Then 0.4 gram of mercuric oxide is added. The foaming which sets in on heating, soon subsides, and the liquid is heated strongly until it becomes water clear. It is necessary to work under a hood if the Vogtherr apparatus is not used, because of the sulfur dioxide liberated, by the reduction of SO_3 by the organic material, particularly at the beginning.

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[40] Jodlbauer, M., *Chem. Zentr.*, **57**, 433 (1886); Krüger, M., *Ber.*, **27**, 1633 (1894).

[41] Wilfarth, H., *Chem. Zentr.*, **56**, 113 (1885).

[42] Zellner, H., German patent 271219 (1914); *Chem. Zentr.*, **85**, I, 1320 (1914).

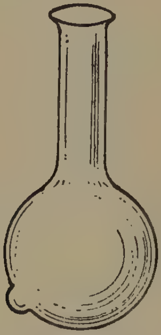

FIG. 176. DIGESTION FLASK FOR MIXTURES THAT BUMP BADLY (MASTBAUM)

Liquid materials are treated in exactly the same way. For example, if 10 cc. of urine is put in the flask, followed by the sulfuric acid which, of course, causes strong heating, and mercuric oxide then added, so much dilute acid is evolved when the flask is heated, that the remainder in the presence of the mercuric oxide, completely destroys the organic material, and at the same time converts all the nitrogen into ammonia.

The heating may be done on the sand bath, on a gauze, or over a small, free flame. If many Kjeldahl determinations are to be run at the same time, a special rack, similar to that shown in figure 177 devised by Taylor, is used.

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[43] Sherman, H. C., *Methods of Organic Analysis*, 2 ed., New York, 1912, p. 292.

The liquid obtained when mercuric oxide is used as catalyst is transferred to a round bottom flask of about 0.75 liter capacity, and the original flask thoroughly rinsed with water to insure quantitative removal of its contents. To this solution is added 80 cc. of 25 per cent sodium hydroxide solution, taking care that at first only so much is added that the liquid which becomes very hot, remains slightly acid. After it has been cooled under the tap, the rest of the caustic soda is added, because now there is very little danger that the ammonia will escape from the alkaline solution. In any case, it is necessary to work rapidly. (See below for the procedure to be used with flasks inclined at an angle.) If the Gunning solution has been used, the method is the same, but more sodium hydroxide solution is needed.

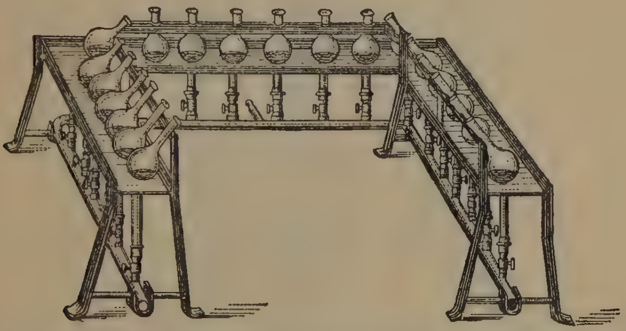

Fig. 177. Taylor's Rack for Kjeldahl Nitrogen Determination

After 1 to 2 grams of zinc dust is put in the flask to eliminate the bumping when the alkaline liquid is boiled, the ammonia is driven over, the condenser being cooled during the first stages only, for reasons given below. The liquid in the flask does not become excessively viscous if the device shown in figure 178 is set on the distilling flask, since it acts as a reflux condenser and also prevents any alkaline liquid spraying over into the receiver. This adapter is about 25 cm. long, and the wide portion about 3.2 cm. in diameter. *A* passes through the stopper of the distilling flask, while *B* leads to the condenser. The lower lateral opening at *A* is particularly effective, because without it the drops which are running back and impeding the passage of the gases, would be continuously thrown back and forth through the whole length of the adapter, but with it, this ceases immediately. There is formed instead, a small column of liquid from which the drops fall, and spurting is thus prevented. The zinc dust cannot be replaced by fragments of granulated zinc,[44] for although this is practically as effective for eliminating the bumping of the boiling alkaline liquid, it is not capable of liberating the small amount of nitrogen which is combined with the mercury as amine-like compounds, whereas this nitrogen is driven over as ammonia in the presence of zinc dust. Consequently, if it is not used, potassium sulfide solution must be added after adding the caustic soda solution, in order to liberate the ammonia from the amine-like mercury compound.

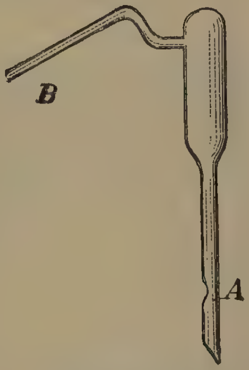

Fig. 178. Distillation Head for Ammonia Determinations (Lassar-Cohn)

Despite all the advantages of the Kjeldahl method, Vogtherr[45] states that it has the indisputable disadvantage of requiring a large installation of apparatus, if a number of determinations must be run simultaneously. Not the least disturbing factor is the tremendous evolution of sulfur dioxide, which is very unpleasant for the operator, and makes the use of a good hood absolutely essential. At present, digestion flasks are used and one or more of them are heated on a sand bath designed for this purpose, but they cannot be used except in a hood or in a well ventilated place. Ordinarily, the sulfuric acid solution is then transferred to a new flask where it is treated with caustic soda solution, and distilled sometimes with and sometimes without steam through a condenser cooled at first. The ammonia formed is absorbed in standard sulfuric acid. In the course of time, various unfortunate occurrences in student laboratories have led Vogtherr to turn his attention to a suitable simplification of the Kjeldahl processes, and he has gradually developed a type of Kjeldahl apparatus in which the digestion of the nitrogenous material may be accomplished without the need of a hood, or a particularly drafty place. The ammonia may be distilled from the same flask. This apparatus which is quite widely used, is arranged as follows:

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[44] Arnold, C., and Wedemeyer, K., *Pflüger's Arch. Physiol.*, **52**, 591 (1893); *Zeit. anal. Ch.*, **31**, 527 (1892).

[45] Vogtherr, M., *Ch. Zt.*, **27**, 988 (1903).

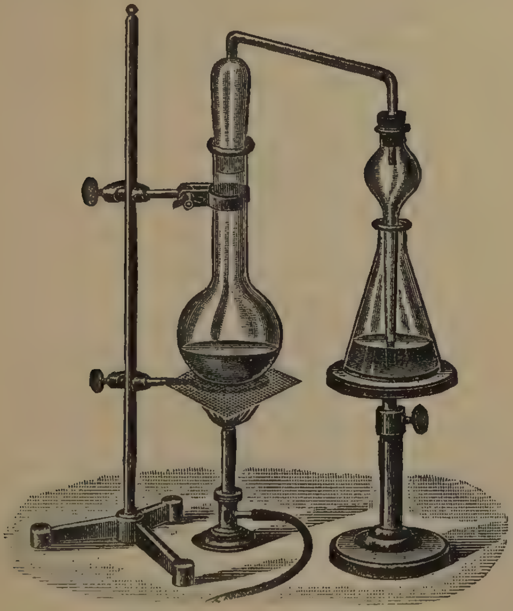

Fig. 179. Kjeldahl Apparatus (Vogtherr)

An adapter continued as a distillation tube bent downward, is ground to fit air-tight the opening of a 500 cc. Kjeldahl flask placed vertically (fig. 179). The distillation tube is bent downward again at right angles, passes through a cork or rubber stopper and opens into the pear-shaped, widened absorption tube, whose lower end dips into the receiver containing the absorption liquid. An Erlenmeyer flask or any other suitable vessel may be used as the receiver. This arrangement serves both for the digestion of the sample with sulfuric acid, and also for the distillation of the liberated ammonia in the following way: The flask is charged with the sample as usual and this is covered with 15 to 20 cc. sulfuric acid, phosphoric-sulfuric acid, phenol-sulfuric acid, etc., and the catalysts added. The distillation tube is put in place and the absorption bulb connected with its free arm extending into a vessel containing sodium hydroxide. On heating, air and sulfur dioxide are driven out; and with much bubbling, the sulfur dioxide dissolves in the caustic soda solution, forming sodium sulfite and sodium bisulfite and none, or practically none of it, escapes into the atmosphere. When the formation of sulfur dioxide is over, the evolution of gas stops, and the receiver containing sodium hydroxide is lowered so that the lower opening of the absorption bulb is above the surface of the liquid. As the heating is continued, the sulfuric acid begins to volatilize; but it condenses in the long neck of the digestion flask and flows back practically without loss, carrying with it the particles of carbon adhering to the walls. After one to two hours heating, the contents of the flask are colorless or pale yellow. The heating is then interrupted, the flask allowed to cool, the adapter and absorption bulb removed, and both rinsed with water till they contain no trace of acid. The contents of the flask are diluted with 100 cc. distilled water, and no anxiety need be felt on the addition of water to the concentrated sulfuric acid because of the excellent quality of the flasks now available. A quantity of 15 per cent sodium hydroxide solution, whose volume is ten times that of the sulfuric acid used, is run into the bottom of the digestion flask through a thistle tube, some zinc or zinc dust added, and the adapter and absorption bulb put in place. The ammonia evolved when the solution is heated is absorbed in standard acid, whose excess is finally determined with standard potassium hydroxide or barium hydroxide. Rosolic acid is used as indicator. The caustic soda solution ought never to spurt over. It is possible to work with 10 sets of this apparatus at one time in the same room, for instance, with no inconvenience from sulfur dioxide.

The ammonia is usually absorbed in a flask which may be closed as shown in figure 180. It contains water to which has been added somewhat more decinormal acid than corresponds to the anticipated ammonia, *i.e.*, usually between 25 to 50 cc. Experience has shown that it takes considerable time before all of the ammonia reaches the receiver. Benedict[46] believes the reason is that the moisture precipitated in the condenser retains the ammonia for a long time in the cold. If, after distilling for 15 minutes through a cooled condenser, the water is run out of it so that the cooling tube becomes hot, and the distillation continued until the contents of the receiver are warm, which requires about five minutes, the last traces of the ammonia will be driven over in this time. Peschek[47] states that the condenser tube must be made of Jena or a similar glass because hot water extracts considerable quantities of alkali from ordinary glass. This evil can be positively avoided by using a tube of block tin.

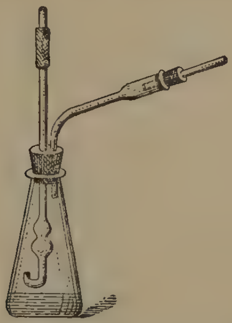

FIG. 180. AMMONIA ABSORPTION FLASK (FRITSCH)

According to Hopkins,[48] losses of ammonia may occur because the quantity of acid requisite for combining with the ammonia does not cover the end of the condenser even though the latter dips into the acid in the receiver. Following this observation, it seems necessary to frequently shake the receiver containing the acid.

Each cc. of decinormal acid used is equivalent to 0.0014 gram nitrogen. The excess acid is titrated with decinormal sodium hydroxide. The writer uses as indicator May's[49] litmus solution, which is prepared as follows: 100 grams of unground litmus is heated to boiling with 700 cc. of water, which is then poured off, and the residue again boiled up with 300 cc. water. The combined extracts are allowed to settle from one to two days, filtered, and the filtrate just acidified with hydrochloric acid. This solution is then dialyzed until hydrochloric acid can no longer be detected in the water, which takes about eight days, if the water is changed frequently. The solution is stored in a flask closed with a plug of cotton. In the course of months it again deposits solids from which it may be filtered, but it remains extremely sensitive to acids and alkalies for years.

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[46] Benedict, F., *J. A. C. S.*, **22**, 259 (1900).

[47] Peschek, E., *J. f. Landw.*, **54**, 367 (1906).

[48] Hopkins, *J. A. C. S.*, **20**, 961 (1898).

[49] Mays, K., *Z. anal. Ch.*, **25**, 402 (1886); see also Rice, E., *J. Ind. Eng. Ch.*, **4**, 229 (1912).

From time to time, statements appear that the Kjeldahl process fails when applied to certain cases. Thus in 1903, Kutscher and Steudel[50] claimed that it could not be used for determining the nitrogen in materials like creatin, lysin and uric acid. Repetition of these analyses to test these striking results by Beger, Fingerling and Morgen[51] showed that the failure was not due to the method but to its improper use.

(α) Simultaneous determination of carbon and nitrogen

Fritsch[52] has devised a procedure for the simultaneous determination of carbon and nitrogen. It is based on a combination of the Messinger method for carbon and of the Kjeldahl method for nitrogen. In discussing the practicability of his method, he states that the procedure involving oxidation with potassium dichromate, which he used in place of chromic acid recommended by Messinger, may be used according to his previous experience, for the determination of carbon in all organic materials. However, it may only be used in the simultaneous determination of nitrogen, when the materials to be analyzed are directly susceptible to the Kjeldahl method as found by Dafert (see page 419).

He carries out the determination of carbon with the aid of the simplified apparatus of Küster and Stallberg. His procedure is as follows: The combustion tube, which has previously been ignited in a current of oxygen, is heated before beginning the weighings. Solid materials are placed in a weighing tube about 20 cm. long, 1 cm. wide, weighed, and the tube then inserted horizontally into the flask up to about the middle of the bulb. The flask is then turned upright and the sample is made to slide out of the tube by tapping, and the tube then reweighed. Liquid materials which are not easily volatile are best weighed in small glass tubes about 2 cm. long and 1 cm. wide, which are then cautiously slid into the flask. Twenty cubic centimeters of concentrated sulfuric acid, free from carbon, is poured into the flask containing the sample, through a long necked funnel with the precaution that the end extends only slightly into the bulb so that spurting is prevented as much as possible, taking care that the walls of the neck of the flask are not wet with sulfuric acid when the funnel is removed.

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[50] Kutscher, F., and Steudel, H., *Z. physiol. Ch.*, **39**, 12 (1903).

[51] Beger, C., Fingerling, G., and Morgen, A., *Z. physiol. Ch.*, **39**, 332 (1903).

[52] Fritsch, P., *Ann.*, **294**, 79 (1896).

The tube that admits the air is then put in place, and the tube containing the finely powdered potassium chromate is attached to its side arm by means of a smooth piece of rubber tubing. The quantity of potassium dichromate, according to Krüger,[53] who also has carefully investigated the determination of nitrogen in derivatives of benzene, pyridine and quinoline by the Kjeldahl method, with simultaneous oxidation of the carbon, should be about 0.5 gram more than has been calculated as necessary for complete oxidation. Fritsch always used 5 grams of dichromate for 0.2 to 0.3 gram of material. The dichromate was purified by three recrystallizations from water, and was then found to be chlorine free.

The flask, charged as above, is then clamped to a stand and connected by a piece of rubber tubing with the U-tube containing glass wool moistened with sulfuric acid. Finally, the potash bulb is connected to the calcium chloride tube and, at the same time, the combustion tube is heated more strongly.

It is not necessary to pass carbon dioxide-free air through the apparatus before attaching the potash bulbs for, assuming that it is filled with air containing carbon dioxide, since the volume of the apparatus—flask to calcium chloride tube—amounts to about 200 cc. the weight of carbon dioxide would only be 0.00012 to 0.00013 gram. This quantity has no influence on the results of the analysis.

The oxidation may now be commenced, while a slow current of air, whose velocity can be regulated by a screw clamp, is passed through the apparatus. The potassium bichromate is made to gradually slide into the flask by tapping on the tube through which the air is introduced. When working with materials which are very easily oxidized, such as hydrogenated isoquinoline derivatives, the flask must be cooled at first by placing it in a beaker of cold water, because in addition to considerable heating of the sulfuric acid solution, mists are frequently formed. The gradual addition of the dichromate should be so regulated that about one-third to one-fourth of it has been shaken in after five minutes. After this, the evolution of carbon dioxide commences to be vigorous and is accompanied by spontaneous heating and by foaming. In the course of the next 10 minutes, the rest of the bichromate is shaken in at such a rate that the generation of gas in the flask remains rather vigorous and uniform. As it subsides, a Bunsen burner fitted with a chimney and burning with a small luminous flame about 1 cm. high, is put under the flask which should have been clamped so that the bottom is about 10 cm. above the top of the burner. The flame is gradually increased as the generation of the gas decreases. The heating is continued until the liquid in the flask has become green and a bright green slimy precipitate of potassium-chromium sulfate begins to separate. The glass wool moistened with sulfuric acid retains the water and any sulfuric acid which may have been carried over. The flame is now removed and a vigorous current of air is passed through the apparatus for about ten minutes longer, and the potash bulb then taken off.

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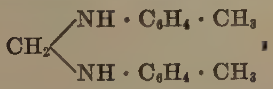
[53] Krüger, Martin, *Ber.*, **27**, 609 (1894).

In order to determine the nitrogen, the residue from the oxidation is washed into a distilling flask. A little of the green precipitate may adhere to the bottom of the flask so firmly that it cannot be rinsed loose by water. However, two or three extractions of this residue with hot water insures complete removal of all the ammonium sulfate. The flask is easily cleaned by warming a little dilute alkali in it, rinsing with water, and then heating with dilute hydrochloric acid. The contents of the distilling flask are diluted with water to about 300 cc., and a nitrogen trap attached, which leads into a condenser connected with the receiver containing a small excess of standard acid and about 50 cc. of water (fig. 181). A few drops of the absorption liquid are gotten into the bend of the tube, provided with a Bunsen valve by swirling the receiver, so that the air which escapes through the tube when the distillation begins, is washed by the diluted standard acid. This device also makes it possible to easily observe the rate of distillation. In order to drive the ammonia out of the liquid in the flask, 80 to 90 cc. of 30 per cent caustic soda solution is then added through a funnel inserted in the tubulure of the nitrogen trap. If the flask is slanted sufficiently, the alkali solution will run down the neck of the flask, and into it without mixing with the contents. After shaking well, which causes the ammonia to be liberated, the distillation is begun with a small luminous flame so that the evolution of the ammonia is not violent, but as uniform as possible. It is well to add zinc dust, even though Fritsch does not prescribe it, to the distillation mixture so that it will not foam. Later, the flame is increased and one-third of the contents of the flask driven over. The Bunsen valve must be removed as soon as the flame under the flask is extinguished. Fritsch used decinormal hydrochloric acid for absorbing the ammonia, and titrated the excess acid with standard barium hydroxide solution in the presence of methyl orange. He claims that after some experience, the whole analysis requires one and one-half hours, distributed as follows:

	minutes
Weighings and assembling of apparatus	15
Addition of one third of the dichromate	5
Addition of two thirds of the dichromate	10
Heating of the oxidizing mixture	15
Aeration	10
Dismantling the apparatus and transfer of the oxidizing mixture to the distilling flask	5
Distillation	15
Back titration	5
Weighing and calculating	10

(*c*) *Will-Varrentrapp method*

The Will-Varrentrapp method is already passing into oblivion, but there are said to be instances in which it alone yields correct analytical results. Thus Grünhagen[54] found that the Kjeldahl method failed when applied to methylene di-*p*-toluidine,



$$\mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{NH\cdot C_6H_4\cdot CH_3}\\ \mathrm{NH\cdot C_6H_4\cdot CH_3}\end{array}\right.,$$

and other closely related bases, although the assumption that its nitrogen is easily convertible into ammonia, is certainly justified.

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[54] Grünhagen, H., *Ann.*, **256**, 289 and 293 (1890).

However, he found as much as 3 per cent too little nitrogen. He had first determined the nitrogen by the Dumas method, which also gave low results. The reason may have been that the residual carbon from the combustion with cupric oxide retained nitrogen, because, when a C + H analysis of the material was carried out in a current of oxygen, it was found very difficult to burn the last particles of the graphite-like carbon which separated. Results agreeing with those calculated could only be obtained by using the Will-Varrentrapp method.[55]

In 1841, Berzelius and Plantamour[56] stated that it seemed possible to convert the total nitrogen content of nitrogenous materials into ammonia, by igniting them with alkalies, and thus determine it. Shortly thereafter, Will and Varrentrapp published their method based on the same assumption. They used soda lime as the fixed alkali. This method cannot be used for nitro bodies.

The soda lime is prepared by adding 2 parts quick lime to a solution of 1 part of caustic soda in water, evaporating to dryness, and gently igniting the residue. The sample to be analyzed is finely ground and mixed with about 10 times its weight of soda lime, and then placed in a combustion tube about 30 cm. long, drawn out to a point at one end. More soda lime is then added. A receiver of the form shown in figure 181, containing dilute hydrochloric acid is fastened to the open end of the tube. The tube is heated in a combustion furnace, beginning at the end nearest the receiver, and working toward the closed end. The ammonia remaining in the tube is drawn into the receiver by connecting the latter with a very feebly acting air pump, and breaking off the point of the combustion tube. Formerly, it was customary to determine the ammonia which had passed into the receiver, as ammonium chlorplatinate. However, it is more convenient to add caustic soda solution and zinc dust to the contents of the receiver and then distil, the ammonia being thus determined volumetrically.

The combustion must not be carried out too rapidly. At the most, one bubble per second should pass the receiver. If the absorbing acid should become turbid or yellowish, the determination should be considered a failure. Not more than 0.5 gram of the material should be used for the analysis, and only 0.3 gram of a substance rich in nitrogen.

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[55] Varrentrapp, F., and Will, H., *Ann.*, **39**, 257 (1841).

[56] Berzelius, J., and Plantamour, P., *J. pr. Ch.*, [1], **23**, 231 (1841).

DETERMINATION OF HALOGENS AND SULFUR

The halogens and sulfur have been included under one heading because many of the quantitative methods of determining these, to be discussed here, are the same as regards the destruction of the organic material by nitric acid or sodium peroxide.

A. Qualitative

(*a*) *Halogens*

Chlorine, bromine and iodine are usually detected qualitatively by heating the material with lime which then combines with the halogen. The residue from the ignition is dissolved by means of water and sulfuric acid, and the halogen identified, as usual, in the filtrate. However, compounds like chlorbenzene, chlortoluene, cannot easily be decomposed by a little lime.

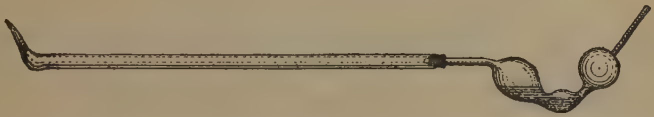

FIG. 181. NITROGEN DETERMINATION APPARATUS (WILL-VARRENTRAPP)

If sodium peroxide is available, chlorine, bromine and iodine are best detected by Pringsheim's[57] method. The procedure is as follows: Some sodium peroxide is weighed, and to it is added one twenty-fifth of its weight of a material containing much carbon and hydrogen, and which is not hygroscopic, such as naphthalene, cinnamic acid, etc. The mixture is kept ready for use in a tightly closed bottle. Enough of the oxidizing mixture to cover the point of a small knife blade is put into an iron deflagrating spoon, thus saving a test tube, and a few grains of the solid to be tested, or a few drops of a liquid sample are added. The mixture is heated in a Bunsen flame until the reaction begins with a pronounced hiss. The spoon is then allowed to cool, and the reaction product dissolved in a little water.

[57] Pringsheim, Hans H., *Ber.*, **37**, 2156 (1904).

The solution is divided into two parts. One is acidified with nitric, the other with hydrochloric acid. One portion of the nitric acid solution is treated with silver nitrate to precipitate the halogens, and another portion is treated with ammonium molybdate to detect phosphorus. The hydrochloric acid solution is tested for sulfur.

Kastle and Beatty[58] oxidized the material to be tested for halogen with a chlorine-free mixture of copper and silver nitrates. This mixture completely oxidizes the organic material, the halogen combining with the silver. About 0.1 gram of the non-volatile material is mixed with 0.5 gram of the oxidizing mixture and heated in a small glass tube, but not above dark redness. The cooled mass is treated with water and dilute sulfuric acid, and a few fragments of zinc then added. After a short time, the filtrate is tested for halogen. The vapors of very volatile materials are led through a small tube suitably bent, over the fused mixture of the nitrates, and the heating continued until there is definite decomposition of the nitrates.

The procedure devised by Beilstein[59] may be carried out with very little material. The halogens are detected by heating the compound with pure cupric oxide held in the loop of a platinum wire, first in the inner and then in the outer flame of a Bunsen burner. A green coloration of the flame shows the presence of halogens, and an idea of the approximate quantity may be obtained by its duration. The reaction may be used with materials as volatile as methyl iodide and chloroform.

(*b*) *For sulfur*

From a qualitative standpoint, it is as important to definitely prove the absence as well as the presence of sulfur, particularly when testing natural substances. Furthermore, it is often desirable to learn whether the sample contains oxidized or non-oxidized sulfur. This may frequently be determined with ease.

The detection of sulfur by means of sodium peroxide will be given later when discussing the use of this reagent for the quantitative determination of halogen. Unless this method is used, it is best to follow Vohl's[60] procedure: The sample is heated with sodium in a small glass tube, the melt dissolved in water, and a solution of sodium nitroprusside added. A blue-violet coloration shows the presence of sulfur.

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[58] Kastle, J., and Beatty, W., *Am. Ch. J.*, **19**, 412 (1897).

[59] Beilstein, F., *Ber.*, **5**, 620 (1872).

[60] Vohl, H., *Z. anal. Ch.*, **2**, 442 (1863); *Dingler. polyt. J.*, **168**, 49 (1863).

Horbaczewski[61] proved the absence of sulfur in elastin, for instance, as follows: 2 grams of this material was dissolved in boiling concentrated potassium hydroxide solution, and an excess of chlorine passed into the cooled solution. An excess of hydrochloric acid was added and the solution boiled until no more chlorine was evolved. The hot liquid was then treated with barium chloride solution, and as no trace of turbidity appeared even after forty-eight hours, the absence of sulfur was established.

Neither of these methods shows the form in which the sulfur is present in the compound being analyzed. This may be determined, according to Vohl, by using the following solution: 1 part of water and 2 parts of pure glycerine are heated to boiling and small quantities of freshly prepared hydrated lime are added until the liquid is completely saturated with it. An excess of freshly prepared hydrated lead oxide or even of litharge is then put in and the suspension boiled gently for a few minutes. The cooled liquid is then poured off from the sediment and stored, protected from carbon dioxide. If materials containing unoxidized sulfur, such as hair, taurine, etc., are heated with this reagent, these compounds are immediately turned black by the lead sulfide which separates; but if the sulfur is present in an oxidized form, no blackening occurs.

B. Quantitative

The complete destruction of the organic material which is absolutely essential for the quantitative determination of the non-metals has long been accomplished in sealed tubes by means of nitric acid as recommended by Carius. Recently, the sealed tube with all its inconveniences, usually has been dispensed with by using sodium peroxide in halogen determinations, and cobalt oxide when determining sulfur. Several other methods which likewise require no sealed tubes will be discussed later. Procedures which may be used only for the halogens, or only for sulfur, will follow.

[61] Horbaczewski, J., *Monatsheft f. Chemie*, **6**, 650 (1885).

(*a*) *Nitric acid procedures*

(α) For halogens

Küster's[62] investigations published in 1895 showed that the Carius[63] method of determining halogens in organic materials is the best, because if properly carried out, it combines unconditional reliability with unusual accuracy, and yet requires but little time. According to his experience, the determinations are carried out best under the following conditions. The tubes to be used should be bomb tubing of Jena or a similar glass. Combustion tubing is not so good and tubes made of soft glass should never be used. The tubes should have 2 mm. walls, about 12 mm. bore, and an original length of about 50 cm. Each usage should not shorten such a tube more than 3 cm. if economy is practised when forming the capillary and when opening the tube, and therefore it may be used ten times or more before its length is reduced to 20 cm. which is the minimum for safe working. Good sealing tubing will withstand this repeated use, while ordinary combustion tubing becomes unreliable after being used only a few times, probably because of a change in the structure of the glass that may be easily detected when sealing the tubes.

The tube is charged with whole pieces of silver nitrate. There is no point in pulverizing it. Ordinarily, 0.5 grams is sufficient and 16 to 20 drops of nitric acid (d. 1.5). This quantity of acid is enough for any case and every drop more only increases the danger that the tube will burst. The acid is dropped directly into the tube held vertically, since a few drops flowing down the inner wall will do no damage.

After the silver nitrate and nitric acid have been put in the tube, a small tube, 9 mm. in diameter, 2.5 cm. long, 0.5 mm. walls, sealed at one end, and containing 0.1 to 0.2 gram of the sample is slid in. The tube is then sealed by forming a thick walled capillary, not too short. It is then wrapped in a sheet of filter paper and placed in a bomb furnace whose iron tubes are not quite horizontal, with the capillary at the higher end. Experience has shown that fewer tubes break when wrapped with paper than when the glass is in direct contact with the iron. The furnace is then heated to 320 to 340° for two hours, not including the time required to reach this temperature. It is not necessary to gradually raise the temperature to its peak, but from the beginning the flames are turned as high as is necessary to reach 320 to 340°. A thermometer filled with nitrogen above the mercury must be used, since above 290° ordinary thermometers do not indicate true temperatures because the mercury begins to boil so that the thread rises suddenly. Two hours heating at the given temperature is, with few exceptions, sufficient to complete the decomposition. Küster found hexachlor-benzene C_6Cl_6 to be a case of this kind. It gave correct figures only after heating at 400° for nineteen hours. Later, Kaufler[64] found that the iodine of β-iodo-anthraquinone is held most firmly, and since very stable iodonitro bodies result from the action of nitric acid, complete decomposition in this case also required a temperature of 400°. (Since this compound volatilizes without decomposition, unsatisfactory results were obtained when attempts were made to determine the halogen by ignition with lime. This same is true for β-brom-anthraquinone).

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[62] Küster, F. W., *Ann.*, **285**, 340 (1895).

[63] Carius, L., *Ann.*, **116**, 1 (1860).

The procedure would be unnecessarily complicated if the tubes were first kept for some time at lower temperatures and then opened to relieve the pressure, resealed, and only then heated to high temperatures to complete the decomposition. If the limits given above are not exceeded with respect to the acid and the sample, it is only rarely that a tube bursts. During all operations the tube must be kept in such a position that the end of the capillary is higher than the bottom piece. The silver compounds will then all collect in the bottom of the tube. After the tube is cooled and opened, its contents are washed into a porcelain dish and any particles which adhere stubbornly to the tube are dissolved in a little ammonia, digesting if necessary, for some time on the water bath. The weighing tube is removed and the contents of the dish are filtered through a porcelain Gooch crucible, washed several times with hot water, and sucked as dry as possible. The crucible is then heated in a Meyer's crucible dryer (see page 383) charged with xylene, and is sure to be so dry after one and one-half hours that a repetition of the drying and weighing appears superfluous.

The following statements concerning the Gooch crucible[65] are due to Paul.[66] The form differs only a little from that of the ordinary crucible (fig. 182). However, it has a flat finely perforated bottom on which a removable perforated plate fits. The crucible may be either platinum or porcelain. It is well to protect the porcelain crucible by heating it on an asbestos board rather than over a free flame. The crucible is prepared for filtering by covering its bottom with a pad of prepared asbestos (see page 225). In order to do this, the funnel is fastened by means of a piece of rubber tubing in a glass funnel which is mounted on a suction flask. The asbestos is shaken in a flask with much water to form a very thin suspension and after starting the pump, this is poured into the crucible in a thin stream.

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[64] Kaufler, Felix, *Ber.*, **37**, 61 (1904).

[65] Gooch, F. A., *Chem. News*, **37**, 181 (1878).

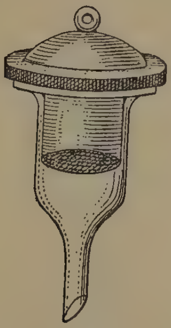

FIG. 182. GOOCH CRUCIBLE

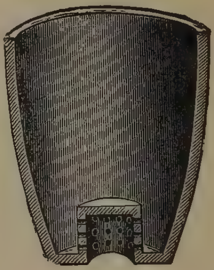

FIG. 183. VOLLERS CRUCIBLE

When the water has run off, the bottom will be found to be covered with a closely knit, uniform mat of asbestos, which should be of such thickness that the holes can no longer be seen when the bottom of the crucible is held toward the light. The perforated plate is then placed in the crucible and more water poured through the filter until it runs through perfectly clear. It is best not to add the water from a wash bottle because of the inevitable spurting which results in the asbestos being stirred up unnecessarily.

Grossfeld[67] states that a mat close enough to retain even freshly precipitated barium sulfate can only be obtained by pouring on the asbestos, a thin suspension of kieselguhr (infusorial earth), extracted with boiling hydrochloric acid. This does not retard the filtration.

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[66] Paul, T., *Z. anal. Ch.*, **31**, 541 (1892).

[67] Grossfeld, J., *Z. angew. Ch.*, **30**, 2, 284 (1917).

Finally the prepared crucible is gradually heated to incipient redness, cooled and weighed. When used for filtration it is again connected with the funnel and suction which must be turned on before any liquid is poured into the crucible. The precipitate should be washed as well as possible by decantation. If the nature of the precipitate permits, large volumes of water may be used, since this runs through the filter with extraordinary speed, and yet perfectly clear. At the end, the precipitate itself is transferred to the crucible and may be dried at any desired temperature. Asbestos is a very excellent filtering material because it is not at all hygroscopic, and a filter dried at 100° weighs just the same after being heated to redness. Since no burning paper comes in contact with the precipitate, the Gooch crucible is particularly suited for filtering silver halides. If used for other precipitates which must be protected from the action of the flame gases, the crucible may be set in a larger crucible of the ordinary type. Of course, a platinum plate with a high edge is still more convenient for this. Vollers[68] has recently modified the crucible by perforating a cylindrical indentation, instead of the bottom (fig. 183). In this way, the articles of the asbestos are prevented from falling out through the holes of the bottom when the crucible is set up.

If, however, silver bromide or iodide is produced in the analysis it is necessary that it be very thoroughly washed by decantation with hot water to remove the excess silver nitrate, because very stable double compounds may be produced. According to Küster, such halogen determinations in experienced hands, yield as an average, results so exceptionally good that there is justification for reporting the result of a single determination to two decimals, although the first decimal place is usually sufficient. But if a mixture of silver chloride and bromide, or iodide is formed, the fusion method of Jannasch and Kölitz[69] should be followed.

Attempts have been made to shorten the final stages of the procedure by using weighed quantities of silver nitrate, and back-titrating the unused portion. However, Küster[70] has shown that the results are poor, indeed often very poor, because considerable quantities of the excess silver nitrate, that has not been converted into silver

[68] Vollers, H., *Chem. Zeit.*, **29**, 1088 (1905).

[69] Jannasch, P., and Kölitz, E., *Z. anorg. Ch.*, **15**, 68 (1897).

[70] Küster, F. W., *Ann.*, **285**, 346 (1895).

halides, reacts with the glass. This quantity, which increases with time and temperature, will not enter into the titration.

If samples of liquids in which the halogen is to be determined, have been weighed in small bulbs, the latter, which eventually must be weighed with the silver halide, must also be made of hard glass. According to Tollens,[71] bulbs made of soda glass give up so much alkali to the nitric acid during the heating, that this also leads to a considerable error.

(β) For sulfur

If materials containing sulfur have been decomposed by this method, the resulting sulfuric acid in the liquid may be determined by the usual method, *i.e.*, boiling hot barium chloride solution is added to the boiling acid solution to produce a precipitate of barium sulfate that filters easily. It is well known, however, that barium sulfate precipitated in the presence of barium nitrate cannot be washed completely. Therefore it is well before precipitating the barium sulfate to drive off the small quantity of nitric acid present, by heating on a water bath. The removal is facilitated by the addition of hydrochloric acid.

In this connection it may be remarked that the determination of sulfate as barium sulfate is regarded by some as obsolescent. The benzidine method is much superior. After much adverse criticism, Raschig, its discoverer, published decisive data about it.[72] Friedheim and Nydegger[73] made valuable contributions as a result of extensive supplementary investigations.

(b) *Sodium peroxide method*

(α) With sodium peroxide solution for sulfur and halogens

According to Modrakowski,[74] the sulfur in liquids, urine for example, may be determined as follows: 1 to 2 grams sodium peroxide is placed in a proper size nickel dish, and 50 cc. urine slowly added, drop by drop. In this way, only moderate foaming follows instead of the spurting that results when the sodium peroxide is shaken into the urine. After evaporating to a syrupy consistency on a water bath, 2 to 3 grams more of sodium peroxide is stirred in gradually. When the action, which is rather violent at first, subsides somewhat, the dish is removed from the water bath, and heated over a small flame until no further evolution of steam can be seen. As a further precaution, it is sometimes advisable to use an alcohol burner because illuminating gas contains sulfur. The heating is then increased with the further addition, if necessary, of 1 to 3 grams sodium peroxide. The mass now forms brown drops and finally becomes viscous. The reaction is then over. After cooling, the residue is dissolved in hot water, filtered, etc. The filtrate must be absolutely water clear, otherwise the barium sulfate will be highly contaminated.

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[71] Tollens, B., *Ann.*, **159**, 95 (1871).

[72] Raschig, F., *Zeit. angew. Ch.*, **19**, 331 (1906).

[73] Friedheim, C., and Nydegger, O., *Zeit. angew. Ch.*, **20**, 9 (1907).

[74] Modrakowski, G., *Z. physiol. Ch.*, **38**, 562 (1903).

(β) With solid sodium peroxide for halogens and sulfur

Pringsheim[75] justly terms his procedure involving sodium peroxide, a rapid method for the quantitative determination of chlorine, bromine and iodine in organic compounds. It, as he emphasizes, is characterized by all the essential advantages of an analytical procedure, such as accuracy, general applicability, rapidity, economy, and cleanliness. After several years' experimentation he has evolved this final procedure.[76] The material to be analyzed is oxidized in an iron crucible with a quantity of sodium peroxide whose weight is calculated by the scheme given below. These materials are mixed by means of an iron nail. The crucible is placed in a dish containing enough cold water to cover the crucible to three-quarters its height. The nail is then held in a flame by tongs, and when red hot is pushed into the reaction mass through a hole in the lid of the crucible.

Materials containing 75 per cent or more carbon + hydrogen + sulfur, require 18 times their weight of sodium peroxide, those with 50 to 75 per cent of these elements, 16 times their weight. Materials with 25 to 50 per cent are mixed with half their weight of a material containing much carbon and hydrogen, and 16 times as much sodium peroxide, while those with less than 25 per cent are mixed with their own weight of the material containing much carbon and hydrogen, and 18 times their weight of sodium peroxide. In this way, the proper proportion between the combustible material and available oxygen is obtained. If too much sodium peroxide is present, the ignition does not extend throughout the whole mass, and if too little is used, the reaction is too violent. If the reaction mass has been fused clear through after the ignition, the combustion has been successful, even though slight traces of carbon remain after the melt is dissolved. (For materials containing arsenic and phosphorus, 50 per cent more sodium peroxide than that calculated by the above scheme, should be used.)

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[75] Pringsheim, Hans, *Ber.*, **36**, 4244 (1903). See also bibliography of fusion methods for sulfur and halogens. Saint Warunis, Th., *Ch. Zt.*, **34**, 1285 (1910); *Ch. Zt.*, **35**, 906 (1911).

[76] Pringsheim, Hans, *Ber.*, **41**, 4267 (1908).

After the crucible has cooled for several minutes, it is laid in water in a dish which is quickly covered with a watch glass. The reaction product dissolves with evolution of the excess oxygen, and the crucible and nail are removed and washed. The resulting solution is turbid because of the hydrated iron oxide derived from the crucible.

(*a*) *Determination of sulphur.* If the sulfur is to be determined, the solution is acidified with hydrochloric acid, which dissolves the iron oxide. Any particles of carbon are filtered off, and the sulfate precipitated by barium chloride.

(*b*) *Determination of halogens.* During the oxidation, there are formed, in addition to the halogen hydrides, oxygenated halogen acids which must be reduced to the former. For this purpose, there is added to the alkaline solution 3 cc. of a saturated solution of sodium sulfite or bisulfite, and dilute sulfuric acid, until the iron oxide precipitate has disappeared. The beaker is covered and the solution heated until the sulfurous acid has been driven off; 3 cc. of concentrated nitric acid is added to keep the silver sulfate in solution, and the halogen is then precipitated by silver nitrate. It is best to weigh the silver halide in a Gooch crucible.

(γ) Determination of halogen by means of metallic sodium and ethyl alcohol

This method, in contrast to the preceding one, requires no special apparatus or reagent, but only material available in every laboratory. As early as 1861, Kekulé[77] determined the halogen in substitution products of the aliphatic series, by splitting off the halogen by several hours action of sodium amalgam and water. Since aromatic compounds do not release the halogen atom when so treated, this method cannot be applied to them. However, Stepanow[78] has worked out the following procedure which is generally applicable.

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[77] Kekulé, Aug., *Ann.*, Supl. I, 133 (1861).

The sample, together with the tube in which it has been weighed, is put into an Erlenmeyer flask containing 20 to 40 cc. of 98 per cent ethyl alcohol. The flask is connected with a rather long condenser, and heated on a water bath. A large excess of metallic sodium is added through the condenser, so that a vigorous reaction is constantly maintained. The quantity of metal should be about 25 times[79] as much as required by the following equation:

$$\mathrm{R{\cdot}Hlg} + \mathrm{C_2H_5OH} + 2\ \mathrm{Na} = \mathrm{R{\cdot}H} + \mathrm{NaHlg} + \mathrm{C_2H_5ONa}$$

After the sodium has dissolved, the contents of the flask are diluted with 20 to 40 cc. of water, and the alcohol distilled off. The liquid is cooled, and dilute nitric acid added until the reaction is strongly acid. The halogen is then titrated by the Volhard method.

Chlorbenzene gave results closely agreeing with the theory. With hexachlorbenzene, the least favorable difference was 0.19 per cent, brombenzene 0.24 per cent, chlornitrobenzene 0.22 per cent. With bromnaphthalene, the differences in 4 determinations were −0.10, +0.03, −0.04, −0.20 per cent.

(*c*) *Chrome-sulfuric acid for determining halogen with and without simultaneous separation of iodine from chlorine and bromine.*

Baubigny and Chavanne[80] determine the halogens by a wet method, with which is combined a separation of iodine from any chlorine and bromine present. They treat the sample with a solution of potassium bichromate in concentrated sulfuric acid. If the material contains chlorine or bromine, these are evolved quantitatively as such, even in the presence of a silver salt, and are collected in a receiver. On the other hand, the iodine is oxidized and retained as iodic acid. They claim that the procedure is very rapid, since not more than 10 minutes is required to oxidize a sample weighing 0.3 to 0.4 gram. Ende[81] has published an excellent treatise on this subject.

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[78] Stepanow, A., *Ber.*, **39**, 4056 (1906); Drogin, I., and Rosanoff, M., *J. A. C. S.*, **38**, 711 (1916).

[79] Van Duin (*Rec. Trav. Chim.*, **45**, 363 (1926)) recommends the use of 50 times the theoretical quantity of sodium, finally heating the mixture to above 100° by a free flame.—H. T. C.

[80] Baubigny, H., and Chavanne, G., *C. r.*, **136**, 1198 (1903).

In a 150 to 200 cc. long neck flask, are placed about 40 cc. sulfuric acid (d.1.84), and a slight excess of silver nitrate, about 1 to 1.5 grams, calculated on the weight of the sample. The salt is dissolved by warming and then 4 to 8 grams potassium bichromate added, which likewise is brought into solution by shaking and further warming. The mixture is allowed to cool, and if iodine is the only halogen present, the sample together with the hard glass tube in which it has been weighed, is put into the flask and thoroughly shaken with the oxidizing mixture. Sometimes the action begins even in the cold, as evidenced by the evolution of carbon dioxide. Often it is necessary to warm at the beginning, but in any case, the contents of the flask must be finally heated to insure complete oxidation. This is accomplished by shaking the flask constantly over a flame, but the temperature should not exceed 150 to 170°. A temperature of 180° should be avoided, because even at that temperature, the dichromate is destroyed by the sulfuric acid without furthering the oxidation. The liberation of free oxygen, shows that the temperature limit has been reached, so that no thermometer is necessary. The flame is then removed and the shaking continued for four to five minutes longer. Iodine vapors appear only when the work is excessively hurried. After cooling, 140 to 150 cc. water is added, and then a concentrated solution of sulfurous acid. This completely reduces the chromic and iodic acids, and the silver iodide precipitates quantitatively.

During the cooling of the aqueous solution, orange colored crystals of silver chromate enclosing silver iodate sometimes separate. This precipitate forms only if too much dichromate has been used. It is easily soluble in nitric acid and consequently, if it appears, a little ammonium nitrate is added and the mixture heated. The solution is then reduced as described above.

If very much sulfurous acid is used, the silver iodide may be slightly gray, because of pulverulent silver resulting from the reduction of silver sulfate. This is removed by treatment with warm dilute nitric acid, either in the flask or on the filter. The published analytical figures indicate very satisfactory results.

[81] Ende, H., *Ch. Zt.*, **35**, 450 (1911); see also Bekk, J., *Ch. Zt.*, **39**, 405 (1915).

It may be added that recently, Vaubel and Scheuer[82] have described a method, somewhat similar to the Kjeldahl process, by which all three halogens may be quantitatively driven into a receiver by heating the organic material with concentrated sulfuric acid.

(*d*) *Determination of iodine in an aromatic compound containing both iodine and bromine*

Auwers and Erggelet[83] had difficulty in determining the iodine content of 3,5,6-tribrom-4-hydroxy xylylene iodide, $Br_3(OH)C_6(CH_2I)_2$, since at first low results were regularly obtained when it was decomposed by digestion with sodium alcoholate in order to determine the iodine. Finally, the determination was successfully accomplished as follows: The iodide was dissolved in acetone, moist silver oxide added, and the mixture warmed in the water bath. The reaction was complete after heating one and one-half hours. The silver iodide was collected on a quantitative filter and washed successively with hot acetone, absolute alcohol, dilute nitric acid and water. The residue was then treated as usual. Grützner[84] has described in detail a procedure for determining minute quantities of iodine in blood and organs.

(*e*) *Further methods of determining sulfur*

(α) For larger sulfur contents

The sulfur of non-volatile compounds can always be converted into sulfate by fusion with potassium chlorate or nitrate together with potassium carbonate, and determined in this form.

The following method appears to the writer to be exceptionally useful because of its convenience. The efficiency of adding cobalt oxide in the combustion of materials difficult to burn has been mentioned in the discussion of ultimate analysis. If sodium carbonate is also added to the mixture of carbon and cobalt oxide mentioned above, the combustion in oxygen is in no wise harmfully affected;[85]

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[82] Vaubel, W., and Scheuer, O., *Ch. Zt.*, **30**, 167 (1906).

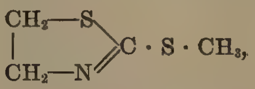
[83] Auwers, K., and Erggelet, R., Fohr, V., *Ber.*, **32**, 3029 (1899).

[84] Grützner, R., *Ch. Zt.*, **38**, 769 (1914).

[85] Brunck, O., *Z. angew. Ch.*, **18**, 1560 (1905); see also Komarowsky, A., *Ch. Zt.*, **32**, 770 (1908).

when completed, the total sulfur of the carbon will be found in the residue as sodium sulfate, and may be weighed as barium sulfate. The best method, also applicable to organic materials of all kinds is, according to Brunck, the following: About 1 gram of finely powdered carbon—correspondingly less of organic materials rich in sulfur should be taken—is thoroughly mixed with 2 grams of a mixture of 2 parts of cobalt oxide and 1 part anhydrous sodium carbonate. The mixing is best done in a glass or a glazed mortar. The mixture is transferred to a large porcelain or platinum boat, and this is pushed into a piece of combustion tubing about 30 cm. long. Oxygen is led in at one end, the other end remaining open. While a moderate current of oxygen is passing through the tube, the far end of the boat is heated with a low flame until the contents commence to glow at this point. The flame is then removed and the glowing is regulated by properly increasing or decreasing the supply of oxygen. Sparking or flaming should not occur. After about fifteen minutes, the cessation of the glowing shows that the reaction is over. The cooled boat and its contents are extracted with warm water to which a few drops of sodium carbonate solution are added, since otherwise the finely divided oxide would pass through the filter. A few cubic centimeters of hydrogen peroxide solution may be added to the alkaline filtrate to insure oxidization of any sulfite present. With varieties of carbon rich in sulfur, the cobalt oxide may easily retain some sulfur in the form of basic cobalt sulfate. Consequently, the precipitate is dried, and after ashing the filter, the residue is dissolved in a little hydrochloric acid, refiltered and treated with barium chloride. The slight precipitate of barium sulfate is added to the main quantity.

When determining the sulfur in μ-methylmercapto-c-thiazolin,



which contains 48.12 per cent sulfur, Gabriel[86] had to heat the sample with fuming nitric acid for three hours at 200°. The resulting liquid was concentrated, neutralized with potassium carbonate, evaporated to dryness, and then fused with sodium carbonate and potassium chlorate. When the fusion was omitted, only about half of the sulfur, namely 25.04 per cent, was converted into sulfate. The other half had obviously gone over into the very stable methyl sulfonic acid. A similar procedure had been described and recommended long before this by Arendt[87] for determining the sulfur content of ashed organic materials.

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[86] Gabriel, S., *Ber.*, **22**, 1154 (1889).

Messinger[88] states that the following method may be used successfully for most, but not all, the less volatile compounds containing sulfur. The weighed sample, together with 1.5 to 2 grams of potassium permanganate and 0.5 gram pure potassium hydroxide, is placed in a 500 cc. flask provided with a reflux condenser. Then 25 to 30 cc. of water is added through the condenser, and the contents of the flask heated for two to three hours. The liquid, which should be slightly red at the end of the operation is cooled and concentrated hydrochloric acid is gradually added through the condenser. After the evolution of gas has ceased, the liquid is heated until it becomes clear. The contents of the flask are then washed into a beaker, and the sulfate precipitated by boiling barium chloride solution.

(β) For small sulfur content

If sulfur is to be determined in materials containing as little of this element as does glue, for instance, the Carius method, according to Krummacher,[89] may not be used, because it permits the use of only relatively small samples. Nor did oxidation fusions yield him satisfactory results. On the other hand, the analyses were easily carried out in compressed oxygen in a calorimeter bomb containing about 10 cc. water.

Goetzl[90] compared all of the methods of determining sulfur in liquid fuels containing little sulfur. (It was shown, for example, that when the Carius method was used, the sealed tubes practically always burst.) He finally evolved the following procedure which satisfied all requirements. It may also be used for detecting small quantities of sulfur, 0.04 per cent for instance, in organic materials of all kinds. The sample, two to three grams of the liquid fuel, is weighed into a large platinum crucible which is covered with a watch glass after the addition of about 4 cc. of fuming nitric acid. After the vigorous initial reaction, the materials are allowed to stand overnight, and the two liquids are then mixed by swirling the crucible. As soon as no more reaction takes place in the cold, the crucible is heated on a slightly warmed water bath, taking care to moderate the reaction by opportune removal of the crucible. When the mass has again become quiescent, the watch glass is again removed and the material evaporated to dryness. Then 6 to 8 grams of a mixture of 10 parts of calcined soda, free from silicates and sulfate, and 2 parts pure potassium nitrate are added, and the whole is mixed by means of a platinum wire, after the mass has been softened again on the water bath.

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[87] Arendt, *Wachstum der Haferpflanze*, Leipzig, 1857, p. 28.

[88] Messinger, Josef, *Ber.*, **21**, 2914 (1888).

[89] Krummacher, O., *Zeit. Biol.*, **45**, 310 (1904).

[90] Goetzl, A., *Z. angew. Ch.*, **18**, 1528 (1905).

Some sodium nitrate is then placed on top and the crucible heated over a free flame and so on.

ASHING

(*a*) *Salts of organic acids*

The ashing of small quantities of salts derived from inorganic bases stable toward heat, as is necessary in the quantitative analysis of these salts, can usually be accomplished without much trouble, in the usual way in a platinum or porcelain crucible, with or without the addition of sulfuric acid. The case is somewhat different when explosive salts are to be ashed. The violence of the reaction may be moderated by mixing in sand. Sometimes they may be converted into non-explosive compounds before the ashing, by fuming off the weighed samples in a crucible with a strong mineral acid or bromine water, etc., before the ignition. For instance, Fischer[91] decomposed the explosive potassium salt of diazoethane sulfonic acid, by evaporating it with dilute sulfuric acid on the water bath, and was then able to ignite the residue as usual.

(*b*) *Plant and animal materials*

(α) By ignition

A much more difficult problem than the preceding one, is the determination of the ash content of organic substances containing salts.

In practically all cases, simple ignition in an open dish does not completely consume the carbon of organic materials containing ash, and consequently, a white ash cannot be obtained in this way. The molten alkali salts envelope particles of the carbon, and protect them from oxidation. Likewise, it cannot be recommended to burn the charred material with ammonium nitrate (Gorup-Besanez), with oxygen, or by fusion with soda and saltpeter (Stahel), because if tolerably large quantities are to be ashed, these aids bring other dangers (spattering), or inconveniences (the considerable amounts of soda and saltpeter). Combustion with potassium nitrate alone is likewise of little use in an exact determination of the ash content. In the presence of such added materials, ignition and particularly strong ignition, may result in loss of ash, because the alkali chlorides volatilize. Furthermore, the ash is not perfectly white, even after strong and long continued ignition. (Graanboom[92] recommends six hours.)

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[91] Fischer, E., *Ann.*, **199**, 303 (1879).

Frequently, the organic material must be broken up before it can be successfully ashed, and Camerer[93] was the first to point out that if it is necessary to finely grind organic material before ashing, fine particles of iron break off from the sharply grooved rolls of the mills, which necessarily raises the weight of the total ash, and also its iron content. Consequently, he allows material pulverized in this way to flow in a thin sheet iron trough over the poles of a magnet, until no more particles are retained. Besides this, he stirs the material with the magnet itself, until the poles remain clean. Tests showed that without this precaution, the iron content of the ash of his samples was as much as 30 per cent too high. The writer believes that when iron determinations in organic materials are to be made that it would be better to grind them between rolls made of phosphor-bronze or other iron-free alloys, instead of between steel rolls.

Ritthausen's[94] special method of determining the total ash in albuminous materials follows. An analysis of the ash itself may not be the main issue, yet this process may find other applications. Although gluten protein materials may be ashed in the usual way, this is not true of plant casein and similar substances, because when they are ashed, the last portions of the carbon which have been enveloped by the molten inorganic constituents, do not burn. After the addition of cupric oxide and iron oxide had been shown to be of little use, as it is very difficult to reoxidize the reduced portions of the oxide, he obtained satisfactory results by using calcium phosphate. This may be easily prepared perfectly pure, and ignited until it is anhydrous. A known weight of the finely powdered casein is intimately mixed with a weighed quantity of the freshly ignited calcium phosphate in a platinum crucible and is then heated for some time, very gently at first, until the organic material is completely charred. It is then ignited at a moderate heat, at last with the crucible loosely covered, until the last trace of carbon has burned, and the residue is perfectly white. After a little practice, this stage may be easily recognized. The increase in weight of the residue over that of the calcium phosphate, equals the weight of phosphate and other constituents of the ash, since during the oxidation, carbon dioxide is not retained, nor does the phosphoric acid volatilize, but is completely retained.

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[92] Graanboom, Dissertation, Amsterdam, 1881.

[93] Söldner, F., and Camerer, W., *Z. Biol.*, **44**, 63 (1905).

[94] Ritthausen, H., *Die Eiweissstoffe der Getreidearten etc.*, Bonn, 1872, p. 239.

Thirty three years later, Gutzeit[95] remarked concerning this procedure, that it could be applied not only to pure albuminous bodies, which after treatment with alcohol could be powdered as finely as desired, but to all vegetable materials, without need of dividing them more finely than usual. For example, he thus determined the ash content of rye straw which had passed a 2 mm. sieve. He found that the calcium phosphate must be weighed rather rapidly, since it attracts moisture. Consequently, it is best to make two weighings, the first to determine the approximate weight, and the second the milligrams, after reheating and then cooling the phosphate. The vegetable material, of which only 0.5 gram was taken in the experiment cited above, was shaken out of the weighing tube into the calcium salt. During the combustion, the platinum crucible was not heated more than was required to make its bottom faintly red so that there was no volatilization of heat stable material. In spite of this, the combustion was finished within an hour, especially when the mass was stirred with a platinum wire from time to time. At the end of each determination, it is best to more strongly ignite the crucible and its contents—about 10 grams—so that after reweighing it and adding more of the material to be investigated, it is ready for immediate use.

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[95] Gutzeit, E., *Ch. Zt.*, **29**, 556 (1905).

Bemmelen[96] has also given a detailed method which is rather inconvenient and unreliable. The very difficult problem of ashing organic materials by ignition has probably been solved by Wislicenus,[97] after a consideration of all the numerous methods proposed. In this, he reverted to the proposal made by Wackenroder[98] to ash the material in the presence of calcium acetate. It is preferable to calcium nitrate which easily causes deflagration and loss of material. Of course, the solution of calcium acetate must be perfectly free from magnesia. Consequently, Shuttleworth[99] first precipitates the iron from a solution of marble in hydrochloric acid, with bleaching powder and then throws down granular calcium oxalate by boiling with oxalic acid. The oxalate is thoroughly washed, dried, and ignited in a muffle. The lime is then dissolved in boiling dilute acetic acid, the solution made up to a definite volume, and the lime content determined. The solution is then diluted so that it will contain about 0.2 gram CaO in each 20 cc. The addition of this material offers a great advantage, since subsequently, the ash is completely decomposible by hydrochloric acid and the expulsion of volatile non metals by silicic acid or by reduction with carbon is avoided. This complete disintegration is sure to be accomplished if, in the first place, there is present from the beginning, an excess of basic material, *i.e.*, if pure lime water or milk of lime, is added along with the calcium acetate solution, even though it becomes saturated, after a time, with carbon dioxide; secondly, if the dry material is actually uniformly moistened before the slow burning. (Leavitt and Le Clerk[100] also found that in the presence of calcium acetate, the loss of phosphoric acid was reduced to a minimum, even when the temperature was carried too high.)

With this preliminary treatment, the first phase of the ashing, the charring, proceeds rapidly, uniformly and without loss. The second phase, the burning of the carbon, is attended by greater difficulties, namely, the complete removal of the carbon and the prevention of any volatilization of the constituents of the ash at red heat. Complete combustion is rather difficult when plant materials are being ashed. It is often possible, under the microscope, to recognize particles of carbon in apparently well burned ash, even though sintering has been avoided by careful heating. Wislicenus had no success when he added the oxidizing agents named above, but accomplished the desired result with hydrogen peroxide, which he was the first to use for this purpose.

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[96] Bemmelen, J. M. van, *Z. physiol. Ch.*, **7**, 505 (1882).
[97] Wislicenus, H., *Z. anal. Ch.*, **40**, 441 (1901).
[98] Wackenroder, H., *Arch. Pharm.*, **103**, 1 (1848).
[99] Shuttleworth, A. E., and Tollens, B., *J. f. Landwirtschaft*, **47**, 183 (1899).
[100] Leavitt, S., and Le Clerk, J., *J. A. C. S.*, **30**, 391 (1908).

High grade hydrogen peroxide can now be obtained on the market. In order to test it, a sample is decomposed with pure platinum black. The original, inherent, slightly acid reaction should disappear. After acidifying with hydrochloric acid and adding barium chloride, a turbidity which is hardly visible and therefore without significance, appears. The 3 per cent solution is used, which avoids the vigorous decomposition by basic materials in the ash. This purest of all oxidizing agents, at the same time, reduces the peroxides of the nonmetals, and consequently, does not overburden the ash with oxygen, but rather has a favorable compensating action. The best procedure is to burn the carbon as much as possible, and then moisten the ash, which always still contains traces of carbon, with 3 per cent solution, and allow it to effervesce slightly. More hydrogen peroxide is then added and the solution slowly evaporated to dryness on the sand bath. The last particles of the ash burn out rapidly and without danger of loss during the careful direct heating which follows, or at least after a repetition of this treatment. The ash will now be found in a uniform, non-compact condition. Only a little of the hydrogen peroxide is lost without acting. During the effervescence it reaches the enclosed carbon, and the oxygen appears to remain in the ash in loose combination until the burning occurs.

The considerable errors which occur during ashing, volatilizing and expulsion of single constituents by others, can, according to Wislicenus, only be avoided by the use of suitable apparatus. The older devices, as well as the one described recently in the German patent 105053, and also its improvements by Tucker,[101] even though very useful, did not satisfy all of his requirements. He was dealing especially with the determination of fluorine in plant ashes, a task which he believes to be one of the most difficult of exact quantitative analysis. While the devices named above were made entirely of platinum, his apparatus was limited to ashing covers for ordinary platinum dishes and platinum crucibles, the latter intended for opening out fusions, without loss.

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[101] Tucker, G. M., *Ber.*, **32**, 2583 (1899).

The upper diameter of the platinum dish should be 7 cm., the lid for this weighs only a little more than 26 grams. The ashing apparatus is shown in actual size in figure 184, and the method of using it is apparent from figure 185. The lid is stiffened by being arched slightly, and by two circular furrows, *a* and *b*, which have other uses. The outer groove, *a*, stiffens the edge and provides a setting for the rim of the dish. The second, *b*, which is curved downward, carries the cylinder, *c*, having a horizontal turned over edge which almost touches the wall of the dish, thus forming the ring shaped space, *d*, in which the entering air is distributed and preheated. Because of this arrangement, the air flows out from the periphery, quietly and uniformly, onto the material, and thus does not blow away the ash. An arch in the lid corresponds to the lip of the dish. The lid is provided with an opening so that oxygen may be mixed with the entering air.

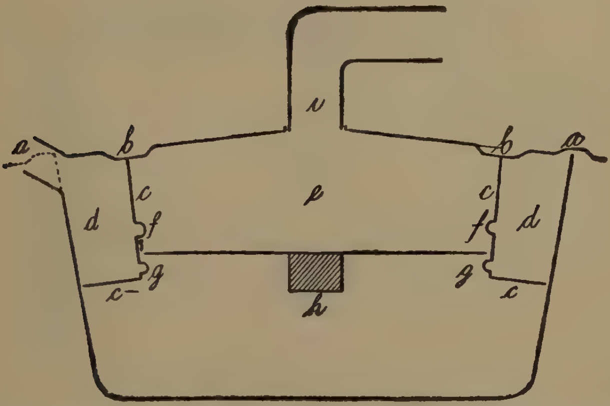

FIG. 184. PLATINUM APPARATUS FOR THE EXACT DETERMINATION OF ASH (WISLICENUS)

The cylinder, *c*, is closed off loosely by a piece of foil. This can be easily set in place, by turning it, and taken out for cleaning by grasping the handle, *h*, made of foil. In the space, *e*, thus formed, are deposited any particles of ash which may have been carried along. The combustion gases escape through the tube, *i*, into which is inserted a well-fitting, hard glass tube, whose end has been drawn out slightly conically for this purpose. This tube is provided with a small condenser, *k*, and forms the connection with the washing vessel, *w*, and through this, with the suction apparatus. The wash bottle charged with glass beads is well suited for the currents of gas being rapidly drawn through it; it breaks them up thoroughly, and completely retains atomized particles of liquid. It is one-third filled with milk of lime or with other basic or carbonate solution. It is clamped in a frame, whereas the condenser is left movable so that by grasping this it is possible, from time to time, to lift the cover from the dish for observation, and to stir the ash. The ash may be turned by a platinum wire bent toward the wall of the dish and inserted through its lip.

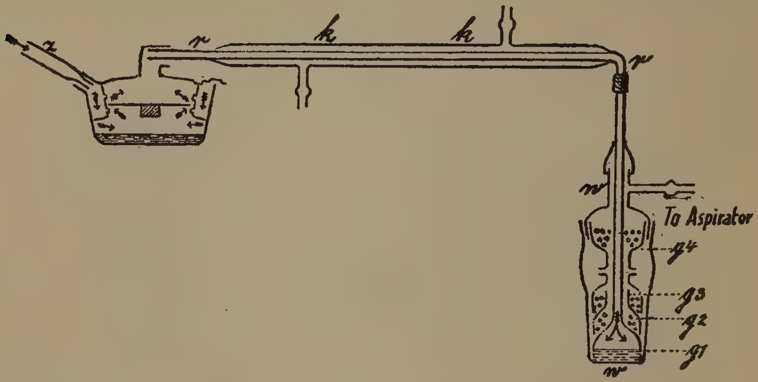

FIG. 185. COMPLETE APPARATUS FOR EXACT DETERMINATION OF ASH

The solution of calcium acetate is used as follows when preparing the ash. For example, 5 to 6 grams of ground oat-straw[102] is placed in a weighed platinum dish and mixed with 20 cc. of the calcium acetate solution and enough distilled water to moisten the whole mass uniformly, and then heated on a water bath, or by some other means until the contents of the dish are dry. The dish is then heated more strongly until the material is ashed. The traces of carbon, carbon dioxide and lime in the 20 cc. of calcium acetate solution are subtracted from the weight of the crude ash to obtain the weight of the carbon-free or pure ash.

[102] Shuttleworth, A. E., and Tollens, B., *J. f. Landwirtschaft*, **47**, 183 (1899).

The volume of calcium acetate solution necessary for a given weight of any material, is determined by experiment. An excess does no harm. For instance, Tollens and Shuttleworth found that 20 cc. was not enough for 3.1227 grams of clover hay, and consequently, 40 cc. was added to the next sample, which weighed 3.8588 grams. This proved sufficient to prevent fusion of the ash. The quantity of calcium oxide necessary appears to depend chiefly on the relative quantities of silica and of alkali present in the ash.

In what follows, dark red heat means that the whole bottom of the dish in which the ash is produced, is heated to this point.

When using the apparatus, it is generally best to weigh the dish with and without the cover, and to make the moisture determination (according to the directions of Wislicenus with 20 to 30 grams) in the dish. The dry substance is then well moistened with a mixture containing equal parts of Shuttleworth's calcium acetate solution and of the purest milk of lime prepared from ignited calcium oxalate. This is then dried on a medium hot sand bath or on a water bath. The material is then charred, but not too rapidly, at first in the open dish fanned with a flame. The dish is then placed in the opening of an asbestos plate (this is also recommended in the patent mentioned above) and fitted with the cover connected to the condenser and wash bottle. The cover should be fitted on loosely so that it can be easily lifted. A moderately rapid current of air is drawn through the wash bottle, which is one-third filled.

The material is ashed as much as possible using, at the highest, a dark red heat, frequently lifting the cover to observe and to turn over the contents of the dish. Just at the end, pure oxygen is mixed with the air for a few minutes and this repeated several times. If the ash is not entirely free from carbon, some pure ammonium nitrate is added, or the oxidation with hydrogen peroxide described above is used, perhaps repeatedly. After each drying, the mass is allowed to burn out in the closed apparatus.

The contents of the wash bottle are then added to the dish, the cover is disconnected from the condenser, inverted on the dish and rinsed out with a little water. Its funnel like form facilitates this operation. The outer edge has, of course, remained clean, and this prevents any loss. As a check, it is weighed after being dried. Figure 186 shows, in actual size, the ashing and fusing apparatus for a platinum crucible.

Tollens[103] drew the following conclusions from his extensive studies of ashing:

1. When ashing organic materials, the ash may sinter or fuse, if too high heat is used.
2. Sintered and fused ashes are not always completely decomposed by hydrochloric acid. As a result, such ashes may yield too high, and varying, percentages of silica.
3. Crude silica obtained from sintered or fused ashes in the usual way, may contain bases chemically combined, probably as double silicates.
4. Calcium acetate solution, if added to the material to be ashed, hinders sintering or fusion even though the material be ashed with strong heating. The lime produced by the ignition facilitates and accelerates the ashing, because it makes the mass less fusible.

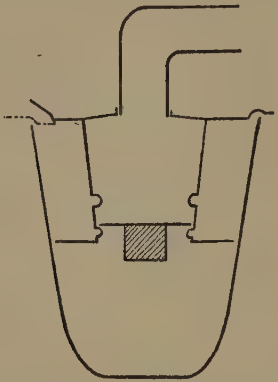

FIG. 186. PLATINUM CRUCIBLE WITH COVER FOR EXACT ASH DETERMINATIONS

5. More or less chlorides are volatilized in the ordinary methods of determining ash.
6. The time required for the ashing by the ordinary methods is unnecessarily long and tedious. If the apparatus discussed is used, and calcium acetate is added, a material may be ashed in less than four hours, without fusion or volatilization.

(β) By the wet method

Neumann[104] achieves the ashing of even large quantities of organic materials in an entirely different way, *i.e.*, by heating them with nitric-sulfuric acid. The solution of the ash obtained does not contain a trace of ammonia and may be used for the qualitative and quantitative investigation of all other bases and for acid radicals, with the exception of the components of the acid mixture. In this method, no charring occurs during the entire course of the destruction of the sample, because a constant supply of an active oxidizing agent continuously oxidizes the carbon completely to carbon dioxide. Since charred masses burn with considerable more difficulty than the original organic materials, this method accomplishes the destruction much faster than dry ashing in a platinum crucible, or than the Kjeldahl digestion.

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[103] Shuttleworth, A. E., and Tollens, B., *J. f. Landwirtschaft*, **47**, 199 (1899).
[104] Neumann, A., *Chem. Zentr.*, **71**, I, 571 (1900).

The ashing is carried out in an inclined hard glass flask of about 500 to 750 cc. capacity, and with a neck about 10 cm. long. A dropping funnel with a capillary opening is placed in a porcelain ring above the flask. A mixture prepared by pouring 500 cc. concentrated sulfuric acid into 500 cc. concentrated nitric acid (d. 1.4) is used.

Solid materials are put directly into the flask, and sticky ones are introduced together with the vessels in which they have been weighed. It is well to previously evaporate to a syrupy consistency materials rich in fat or carbohydrates, such as milk, after adding a 1 per cent solution of pure potassium hydroxide, since otherwise, foaming or bumping of the liquid is apt to occur. For example, 15 cc. of 1 per cent caustic potash solution is added to 25 cc. of milk.

Ashing by means of an acid mixture should be conducted in a hood that draws well. The sample, in a round bottom flask, is covered with 5 to 10 cc. of the acid mixture, and heated with a moderate flame. As soon as the liberation of the brown nitrous vapors decreases more of the acid mixture is run in from the dropping funnel, and this is continued until the reaction begins to slacken, and the intensity of the brown vapors appears to have lessened. In order to determine whether the destruction of the material is finished or not, the addition of the mixture is interrupted for a short time, but the heating continued until the brown vapors have disappeared, and it is noted whether the liquid in the flask becomes darker or even blackens. If this is the case, more of the acid mixture is added, and this test repeated after several minutes. The ashing is completed when the bright yellow or colorless liquid no longer darkens on further heating, without addition of acid and when no more gas is liberated. If the liquid is faintly yellow, it will become perfectly water white on cooling. A volume of water three times that of the acid used is now added and the solution boiled five to ten minutes. Brown vapors derived from the decomposition of the nitrosyl sulfuric acid formed will be evolved. According to Neumann, this acid method of ashing is particularly useful in detecting very small quantities of a constituent of an ash, such as iron in urine, phosphorus in a proteid containing but little of this element, since large quantities of these materials must necessarily be ashed. In the reference cited, he also gives details concerning the method he used for determining iron, phosphate, chlorine as well as hydrochloric acid, potassium, sodium, calcium and magnesium, in the strongly acid solution obtained. The hydrochloric acid was determined by passing the vapors evolved through a solution of silver nitrate.

Lockemann[105] has also given very extensive directions for the destruction of organic material, particularly beef flesh, by means of a mixture of 10 parts fuming nitric acid and ½ to 1 part of concentrated sulfuric acid, of which mixture 5 cc. is enough for 20 grams of flesh.

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[105] Lockemann, *Z. angew. Ch.*, **18**, 421 (1905).

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